CHAPTER II

Chemicals and Instrumental studies
Introduction

The methodology utilized for the mesogenic materials that exhibit enantiotropic nature is attributed by polarizing optical microscope studies. The thermodynamic properties of the phases are studied with emphasis on convinced transition temperatures, enthalpy in heating and cooling cycle by differential scanning calorimetry thermograms. The infrared spectral studies of the functional groups are attributed by recorded infrared spectra in KBr pellet. The structural studies of the synthesized compounds are attributed by $^1$H NMR and $^{13}$C NMR studies recording in CDCl$_3$.

II. 1. Chemicals

The chemicals 4-butyl aniline, 4-decyl aniline, 4,4’-dihydroxy biphenyl, 1-bromodecane, dibromo alkanes, 4-hydroxy benzoic acid, Isophthalic acid, 4-hydroxy benzaldehyde, 4-nitrophenol, 4-benzylxy phenol, dicyclohexylcarbodiimide, N,N’-dimethylaminopyridine, were obtained from Aldrich and sodium nitrite, potassium carbonate, sodium sulphate, phenol, sodium hydroxide, acetone, butanone, tetrahydrofuran, absolute ethanol and dichloromethane were obtained from local company. The solvents were dried and distilled by conventional methods before use.

II. 2. Polarizing Optical Microscope

Microscopic observations of liquid crystal textures can reveal a great deal of information about molecular ordering. To understand the liquid crystal textures, one needs to understand the basic principles of light propagation in anisotropic media. The mesogenic structures are characterized by their textures. This method uses a polarizing optical microscope to view a sample through crossed polarizing
filters. An isotropic liquid, provided it is not chiral, will not interact with the light beams passing through the sample. Thus all the light will be extinct, resulting in a black picture. Liquid crystal phases, however exhibit a phenomenon called birefringence. Due to the anisotropic nature of the molecules, they have two different diffraction indices. Thus, light which is polarized perpendicular to the director \( \mathbf{n} \) passes the mesophase with a different speed than the light which is polarized parallel to the director \( \mathbf{n} \). As a result, the light is split up into a faster and a lower ray, leading to a phase difference upon recombination. Consequently the polarization state of the light is changed while passing through the mesophase and the image does not appear black anymore, as not all light is extinct. Different types of liquid crystal phases show different characteristic optical textures.

The structures were identified using (Leitz DMRXP or Leica DMLP) equipped with a programmable hot stage (Mettler FP90 or FP82HT).

A small quantity of synthesized sample is placed in the slide inserted into a hot stage with temperature varying from room temperature to its isotropic state. The textural observations are observed in both heating and cooling cycles.

**II. 3 Infra Red Spectroscopy**

The confirmation of the functional group of the synthesized compounds is realized by FTIR. Infrared spectroscopy is a chemical analytical technique, which measures the infrared intensity versus wavelength or the wave number of light. Infrared refers to that part of the electromagnetic spectrum between the visible and microwave regions. Based on the wave number, infrared light can be categorized as far infrared (4-400cm\(^{-1}\)), mid IR (400-4000cm\(^{-1}\)) and near infrared (4000-14,000cm\(^{-1}\)). The mid infrared region is of special interest to identify the
functional groups and fingerprint regions. IR spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy.

The most qualitative die press method is generally employed for the purpose of powder sample. The powder is pressed in to pellet. The diluent used is Potassium Bromide. A small amount of powdered sample (1mg) is mixed with KBr powder (50 mg) and grinded for about 5 minutes. The die set is assembled and pressed for about 2 minutes to form a pellet. The IR spectra of all the compounds were recorded on Perkin-Elmer Spectrum 1000 FT-IR spectrometer [1].

II. 4. Differential Scanning Calorimetry

The method for determining mesomorphic properties involves the use of thermal analysis equipment. As heat is required to induce phase transition between two phases having different levels of order, determining this heat can be useful for detecting phase transitions. Differential Scanning Calorimeter is used for the calorimetric thermal analysis. The heat of transition is measured and recorded. This method provides the enthalpy of phase transitions which cannot be obtained by polarizing optical microscope. This is achieved by slowly heating the sample and an inert reference at the same time with the same heating rate. The inert reference should not show any phase changes within the experimental temperature range. When the examined sample melts for example, energy required, resulting in a peak in the DSC plot. The size of this peak is proportional to the enthalpy change of the process. The transitions from crystal to liquid crystal, one liquid crystal phase to another or liquid crystal to isotropic liquid can be detected.
Depending on the amount of change in order during the process, the enthalpy will be greater or smaller.

A liquid crystalline sample in weight range 1-5mg is taken in \( \text{Al}_2\text{O}_3 \) crucibles. For maintaining inert atmosphere high pure nitrogen gas and pure zero air for oxidative atmosphere with 40ml/min were used. The DSC was calibrated by using standard reference material like Indium and Zinc. The thermograms of samples were recorded in both heating and cooling in the temperature ranges 20-250°C at a rate of 10°C/min. Perkin Elmer DSC7 was used for the thermal analysis.

II. 5. Proton Nuclear Magnetic Resonance:

This technique is used to obtain the structural information about molecules due to the chemical shifts. The number of signals in NMR spectrum reveals the number of sets of equivalent protons in a molecule. The position of signals helps to know the nature of protons (aromatic, aliphatic, adjacent to electron withdrawing or electron donating etc.). The type of protons have different electron environment and hence absorb at different applied field strengths. NMR signal is plot with magnetic field strength increasing to the right. NMR spectra are recorded in solution and solvent protons must not be interfering with the sample protons. Hence a large range of deuterated solvents especially deuterated chloroform (CDCl₃) is used. The chemical shift is reported as a relative measure from some reference resonance frequency. TetraMethylSilane is commonly used as a reference. The signals can be singlet, doublet, quartet, sextet and multiplet. The splitting of signal is due to different environments of absorbing protons.
The NMR spectra were recorded on the Bruker AMX-400 (400 MHz) spectrometer or Bruker Aveance series DPX-200 (200 MHz) spectrometer. Once a strong magnetic field is applied the nucleus reorients their spins i.e. aligned with the field or against the field. Orientation parallel to alignment of applied force is lower in energy. When nuclei are irradiated with radio frequency radiation the lower energy nuclei flip to high state and nuclei said to be in resonance, hence the term nuclear magnetic resonance. $^1$H NMR identifies the H atoms present in the compounds.

II. 6. $^{13}$C NMR:

It is the application of nuclear magnetic resonance spectroscopy to carbon. It is analogous to $^1$H NMR and allows the identification of carbon atoms in an organic molecule. It detects only the $^{13}$C isotope of carbon whose natural abundance is 1.1%, because the main carbon isotope $^{12}$C is not detectable by NMR since it has zero net spin. Couplings between carbons can be ignored due to the low natural abundance of $^{13}$C. Hence in contrast to typical proton NMR spectra which show multiplets for each proton position, carbon NMR spectra show a single peak for each chemically non-equivalent carbon atom.

It follows the same principle as those of $^1$H NMR although the typical range of chemical shifts is much larger than for $^1$H NMR. The chemical shift reference standard for $^{13}$C is the carbon in TetraMethylSilane. $^{13}$C NMR provides information concerning the different types of carbon atoms present in the molecule, the electronic environment of the different types of carbons and the number of neighbors a carbon has [2].
References
