CHAPTER 2

INSTRUMENTAL TECHNIQUES AND THEORITICAL CHARACTERIZATION OF LC

2.1 MATERIALS USED

Suberic acid (SA), Azelic acid (AC), Pimelic acid (PA), dodecane dicarboxlic acid (DDC) and p-nOBA are supplied by Sigma Aldrich (Munich, Germany). N, N-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), Methanol (MeOH), Ethanol (EtOH), benzene, Pyridine and dichloro methane solvents used are of high-performance liquid chromatography (HPLC) grade.

2.2 EXPERIMENTAL CHARACTERIZATION TECHNIQUES

The synthesized LC mesogens are characterized by various experimental methods such as spectral, thermal and optical techniques. The structural characterizations of LC are done by FT-IR and $^1$H-NMR, which revealed the presence of hydrogen bond and its environment in the mesogen. The thermal characterization is carried out using DSC which examines the existence of mesophase, melt and isotropic temperatures of LC material, thermal span of the phases and its transition temperatures along with the enthalpy values. The optical characterization is carried out using POM equipped with precision temperature controller which implies the tilt angle of the mesogens. The equipments used for chemical and physical characterization of LC materials are discussed and given in Table 2.1.
Table 2.1 Details of Instruments

<table>
<thead>
<tr>
<th>Instruments Used</th>
<th>Model / Specification</th>
<th>Make</th>
<th>Aim of study</th>
</tr>
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<tbody>
<tr>
<td>FT-IR - ABB Bomem</td>
<td>MB3000</td>
<td>Burlington, Canada</td>
<td>Structural and HB confirmation</td>
</tr>
<tr>
<td>NMR</td>
<td>Ultra Shield 300MHz</td>
<td>Burker, USA</td>
<td>Structural confirmation of molecules</td>
</tr>
<tr>
<td>POM</td>
<td>E600WPOL</td>
<td>Tokyo, Japan</td>
<td>Textural observation, optical tilt angle measurement</td>
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<tr>
<td>Nikon CCD System Digital Sight</td>
<td>DS-U1</td>
<td>Tokyo, Japan</td>
<td>To record the textural images</td>
</tr>
<tr>
<td>Instec hot and cold Stage</td>
<td>HCS 402 STC 200</td>
<td>Instec, USA</td>
<td>Temperature monitoring and controlling</td>
</tr>
<tr>
<td>DSC</td>
<td>DSC60, Shimadzu</td>
<td>Tokyo, Japan</td>
<td>Evaluation of transition temperatures and enthalpy</td>
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<tr>
<td>UV/Vis spectrometer</td>
<td>Lambda 35</td>
<td>Massachusetts, USA</td>
<td>To measure the stability of the compound</td>
</tr>
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</table>

2.3 THEORETICAL METHODS

Experimentally obtained and characterized mesogenic structures have been confirmed through DFT computations which is performed using Gaussian 03W (Frisch et al 2003) program package with B3LYP level with standard 6-311G(d, p) basis set through various studies (Becke 1988, Lee et al 1988). The molecular structure conformations, electronic properties, solvent effect on inter-molecular HB of n-OBA and SA complexes have been computed and analyzed. The harmonic vibrational frequencies, NBO analysis, MEP surfaces are also studied to elucidate the IMHB interactions of supramolecular hydrogen bonded benzoic acid LC. Electronegativity ($\chi$), ionization potential (IP), electron affinity (EA), softness (s), chemical hardness (\(\eta\)) and electrophilicity index (\(\omega\)) of these LC materials are
calculated and interpreted using of HOMO and LUMO energies. The mesomorphic behavior and the nematic phase stabilities for each molecule have been predicted using calculated local charge distribution. UV Stability of the LC is determined through TD-DFT and NLO properties are also calculated for these LC materials.

2.3.1 Optimization Method

The geometry optimization (Becke 1993) has been performed using B3LYP/6-311G (d, p) basis set. The optimized geometry is determined by minimizing the energy with respect to all geometrical parameters without imposing molecular symmetry constraints. Optimized geometry is visualized by Chemcraft software and Gauss view software. The frequency analysis helps to check the presence of any imaginary frequency and to evaluate the zero point corrections. In all the computations unrestricted open-shell approach is adopted.

2.3.2 Super Molecule Method

The interaction energy during mesogen formation through the hydrogen bonded interface is calculated by super molecule method (Van Duijneveldt et al 1873, Hobza & Zahradnik 1988), where these energies are corrected for BSSE by applying CP procedure (Bader 1990 and Strittmatter et al 2000) given in equations (1.2), (1.3) and (1.4).

2.3.3 Harmonic Vibrational Frequencies

The harmonic vibrational wavenumbers are calculated using the similar level of theory. Further, the calculated vibrational wavenumbers are scaled down using the scaling factor 0.9608 to offset the systematic error

2.3.4 NBO

NBO calculations (Glendening et al 1998) have been performed using NBO 3.1 program (G 03 package). The intermolecular delocalization or hyperconjugation leads to various second order interactions between the filled orbitals of one subsystem and the vacant orbitals of another subsystem. The hyperconjugative interaction energy is inferred from the second-order perturbation approach $E(2)$ as follows (Chocholousova et al 2004):

$$E(2) = -n_\sigma \frac{\langle \sigma | \hat{T} | \sigma \rangle^2}{\varepsilon_{\sigma} - \varepsilon_{\sigma^*}} = -n_\sigma \frac{F_{ij}^2}{\Delta E}$$

(2.1)

Where $\langle \sigma | \hat{T} | \sigma \rangle^2$ or $F_{ij}^2$ is the Fock matrix element between i and j is NBO orbitals, $\varepsilon_{\sigma}$ and $\varepsilon_{\sigma^*}$ are the energies of $\sigma$ and $\sigma^*$ NBO’s, and $n_\sigma$ is the population of the donor $\sigma$ orbital.

2.3.5 MEP

MEP is useful quantity to illustrate the charge distributions of molecules and used to visualize variably charged regions of a molecule. Therefore, the charge distributions can give information about how the molecules interact with another molecule. The MEP is widely used as a reactivity map displaying most feasible regions for the electrophilic attack of charged point-like reagents on organic molecules (Xavier et al 2012). The MEP $V(r)$ is created in the space around a molecule by its nuclei and electrons is well established as a guide to molecular reactive behavior. It is defined by Politzer & Truhlar (1981):
\[ V(\mathbf{r}) = \sum A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \]  

(2.2)

where \( Z_A \) is the charge of nucleus A, located at \( \mathbf{R}_A \). \( \rho(\mathbf{r}') \) is the electronic density function for the molecule and \( \mathbf{r}' \) is the dummy integration variable. At any given point \( \mathbf{r}(x, y, z) \) in the vicinity of a molecule, the MEP, \( V(\mathbf{r}) \) is defined in terms of the interaction energy between the electrical charge generated from the electrons of molecule and nuclei (Politzer et al 1985). To predict the reactive sites for electrophilic and nucleophilic attacks for the investigated compounds, the MEP surface have been generated from the optimized geometry.

### 2.3.6 Frontier Molecular Orbitals (FMOs) and Chemical Reactivity

The Highest Occupied Molecular Orbitals (HOMO) and Lowest–Lying Unoccupied Molecular Orbitals (LUMO) are named as FMOs. The energy gap between the HOMO and LUMO is the critical parameters in determining molecular electrical transport properties and measuring of electron conductivity. The HOMO – LUMO analysis has been carried out to explain the charge transfer within the molecule. The \( \eta \), the chemical potential (\( \mu \)), the softness (\( s \)) and the electrophilicity index (\( \omega \)) of all the three title compounds have also been evaluated as follows:

Electronegativity (\( \chi \)): \( \mu \approx -\chi = -\frac{(\text{IP} +\text{EA})}{2} \)  

(2.3)

Hardness \( \eta \approx \frac{(\text{IP} -\text{EA})}{2} \)  

(2.4)

Softness \( S = \frac{1}{2 \eta} \)  

(2.5)

Electrophilicity index \( \omega = \frac{\mu^2}{2 \eta} \)  

(2.6)
where IP is ionization potential, EA is electron affinity of the molecules. The ionization energy and electron affinity can be expressed through HOMO and LUMO orbital energies as $\text{IP} = -E_{\text{HOMO}}$ and $\text{EA} = -E_{\text{LUMO}}$.

### 2.3.7 Solvent Effect

Solvent effects have been computed in the frame work of self-consistent reaction field polarizable continuum model (Miertsu et al 1981, Miertsu& Tomasi 1982, Cossi et al 1996 and Barone et al 1998 (SCRF-PCM) implemented in the G03 code. Single point estimation of the solvation energy is sufficient to pronounce the behavior of the studied systems in benzene, acetonitrile and EtOH since they are characterized by conformational rigidity.

### 2.3.8 Mulliken Population Analysis

The Mulliken populations show one of the simplest pictures of charge distribution and it provides net atomic populations in the molecule. The absolute magnitude of the atomic charges has little physical meaning; Charge distributions of the molecules have been calculated by performing Mulliken analysis. The nematic phase stability has been predicted through the calculated local charge distributions.

### 2.3.9 TD-DFT

TD-DFT is relatively recent. It has been developed by Runge & Gross (1984) who gives a generalized Hohenberg-Kohn-Sham formalism to time-dependent systems. TD-DFT is the natural extension of DFT and often called as “excited-state density functional theory”. Most of the developments and uses are achieved within a linear-response theory, which is enough to
remarkably reproduce the behaviour of most of the physical systems (e.g.,
UV/visible absorption).

UV–Visible spectra of mesogens in gaseous phase, ethanol and
benzene have been simulated using the time dependent density functional
theory (TD-DFT) B3LYP 6-311G (d,p) method. Theoretically predicted UV–
Visible spectra of mesogen are compared with the observed experimental
results and discussed.

2.3.10 NLO

The material is incident with the intense laser beam responds in a
“nonlinear fashion”. It causes the generation of optical frequencies that is
initially absent. This effect allows the production of laser light. So the
applications of NLO are important from basic research to spectroscopy,
telecommunications and astronomy.

The DFT has been used to calculate the dipole moment ($\mu_{dm}$), mean
polarizability ($\alpha$) and the total first static hyperpolarizability ($\beta$) (Wagener
et al 1995) for these molecules in terms of $x$, $y$, $z$ components as per
following equations (2.7), (2.8) and (2.9) respectively.

\[ \mu_{dm} = \left( \mu_x^2 + \mu_y^2 + \mu_z^2 \right)^{1/2} \]  \hspace{1cm} (2.7)

\[ \alpha = \frac{1}{3} \left( \alpha_{xx} + \alpha_{yy} + \alpha_{zz} \right) \]  \hspace{1cm} (2.8)

\[ \beta_{tot} = \left( \beta_x^2 + \beta_y^2 + \beta_z^2 \right)^{1/2} \]  \hspace{1cm} (2.9)

(or)

\[ \beta_{tot} = \left[ (\beta_{xxx} + \beta_{xzy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzx} + \beta_{yxz})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \right]^{1/2} \]  \hspace{1cm} (2.9)
The β components of Gaussian output are reported in atomic units and therefore the calculated values are converted into esu units (1 a.u. = 8.3693 × 10^{-33} esu).