SYNTHESIS, CHARACTERIZATION, OPTICAL, THERMAL BEHAVIOUR AND DFT INVESTIGATION OF NON-CONVENTIONAL LIQUID CRYSTALS

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SYNTHESIS, CHARACTERIZATION, OPTICAL, THERMAL BEHAVIOUR AND DFT INVESTIGATION OF NON-CONVENTIONAL LIQUID CRYSTALS

by

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%	Percentage
^{13}C-NMR	Carbon nuclear magnetic resonance
1D	One dimensional
^{1}H-NMR	Proton nuclear magnetic resonance
2D	Two dimensional
A	Electron affinity
ATR	Attenuated total reflectance
B97X-D	Hybrid functional
°C min^{-1}	Degree Celsius per minute
$CDCl_3$	Deuterated chloroform
CHN	Carbon, Hydrogen and Nitrogen
cmc	Critical micelle concentration
$C_nH_{2n+1}Br$	Bromoalkane
COSY	Correlation spectroscopy
Cr	Crystal
d	Doublet
DCC	*N,N*-Dicyclohexylcarbodiimide
DCM	Dichloromethane
DFT	Density functional theory
DM	Dipole moment
DMAP	Dimethylaminopyridine
DSC	Differential scanning calorimetry
δ/ppm	Chemical shift in part per million unit

EtOH	Ethanol
eV	Electronvolt
Ɛ	Epsilon
FT-IR	Fourier transform infrared
FT-NMR	Fourier transform nuclear magnetic resonance
HMQC	Heteronuclear multiple quantum correlation
HOMO	Highest energy molecular orbital
I	Ionization energy
I	Isotropic
kJ mol^{-1}	Kilojoule per mole
KOH	Potassium hydroxide
LCs	Liquid crystals
LUMO	Lowest energy molecular orbital
m	Meta
m	Multiplet
MeOH	Methanol
mW	milliWatts
MW	Molecular weight
N	Nematic
n	Number of carbon atoms
N_C	Columnar nematic phase
N_D	Discotic nematic phase
N_D*	Cholesteric phase
N_L	Lateral nematic phase
o	Ortho

p	Para
POM	Polarizing optical microscopy
ppm	Part per million
S	Global softness
s	Singlet
Sm	Smectic
t	Triplet
T_{max}	Maximum curing point
TMS	Tetramethylsaline
ΔH	Enthalpy change
η	Global hardness
θ	Theta
ν/cm^{-1}	Wavenumber in centimeter unit
χ	Electronegativity
ω	Omega

SINTESIS, PENCIRIAN, SIFAT OPTIK, SIFAT TERMAL DAN KAJIAN DFT BAGI HABLUR CECAIR BUKAN KONVENSIONAL

ABSTRAK

Dua siri homolog sebatian diimina dan tetraimina telah berjaya disediakan dan dicirikan. Analisis unsur (analisis mikro CHN), teknik spektroskopi FT-IR, 1D, dan 2D-NMR digunakan untuk menerangkan tentang struktur molekul sebatian yang telah disintesis. Sifat hablur cecair dan kelakuan terma semua sebatian telah dijalankan dengan menggunakan POM dan DSC. Homolog dalam siri pertama terdiri daripada sebatian berbentuk V (**3a-3g**) yang terdiri daripada teras fenil pusat yang disambungkan oleh dua unit mesogenik yang sama yang mempunyai ikatan imina (C=N) dan ester (COO) bersama dengan rantai alkoksi terminal , ($-OC_nH_{2n+1}$) dengan n = 6-12. Sebatian rantai yang lebih pendek (n = 6 dan n = 8) menunjukkan fasa nematik monotropik, manakala sebatian dengan rantai alkoksi yang lebih panjang (n = 10 dan n = 12) mempamerkan fasa nematik enantiotropik. Walau bagaimanapun, sebatian dalam siri pertama dengan rantai alkil terminal beranggota ganjil tidak mempamerkan mesofasa. Siri kedua ialah analog oligomer berasaskan benzidin yang mempunyai empat lengan mesogenik (hablur cecair berbilang lengan). Empat rod simetri seperti unit yang mengandungi imina C=N mempunyai rantai alkoksi terminal C_nH_{2n+1} yang mana n juga berjulat dari 6 hingga 12 (**4a-4g**). Apabila memanaskan molekul yang mengandungi n = 8-10 dan n = 12 mempamerkan ciri puncak endotermik peralihan kristal-mesofasa sebagai tambahan kepada subfasa kristal-kristal. Molekul oligomer benzidin simetri tetra-tertukarganti dengan bilangan ganjil nombor karbon rantai alkoksi mempunyai suhu pengawetan yang lebih rendah berbanding dengan pariti genap. Dalam kedua-dua sebatian ganjil dan genap analog, suhu pengawetan berkurangan apabila n meningkat. Pengoptimuman struktur geometri bersama-sama dengan kekerasan global η (dalam eV), kelembutan global S (dalam eV^{-1}), elektronegativiti χ (dalam eV), dan momen dwipolar (DM, dalam Debye) oleh molekul berbilang lengan dengan panjang rantai karbon terminal berubah-ubah telah dinilai juga menggunakan pengiraan Gaussian pada tahap ωB97X-D/6-311+G(d,p) dan ωB97X-D/6-31G(d). Berdasarkan pengiraan, empat lengan yang sama telah distabilkan oleh ikatan hidrogen molekul. Walau bagaimanapun, panjang rantai alkoksi tidak mempengaruhi HOMO-LUMO pada geometri molekul yang dioptimumkan.

SYNTHESIS, CHARACTERIZATION, OPTICAL, THERMAL BEHAVIOUR AND DFT INVESTIGATION OF NON-CONVENTIONAL LIQUID CRYSTALS

ABSTRACT

Two homologues series of diimine and tetraimine compounds have been successfully prepared and characterized. Elemental analysis (CHN microanalysis), FT-IR, 1D, and 2D- NMR spectroscopic techniques were employed to elucidate the molecular structures of the synthesized compounds. The liquid crystal properties and thermal behavior of all compounds were conducted by using POM and DSC. The first series comprising of homologous V-shaped compounds (**3a-3g**) consist of a central phenyl core connected by two identical mesogenic units which possess the imine (C=N) and ester (COO) bonds along with the terminal alkoxy chain, ($-OC_nH_{2n+1}$) where n = 6-12. The shorter chain compounds (n = 6 and n = 8) were monotropic nematic phase, while the compounds with longer alkoxy chain (n = 10 and n = 12) exhibited enantiotropic nematic phase. However, compounds in the first series with the odd-membered terminal alkyl chain were found to be non-mesogenic in nature. The second series of benzidine-based oligomers possess four mesogenic arms (multi-arm liquid crystal). The symmetrical four rod like imine C=N containing units possess terminal alkoxy chains C_nH_{2n+1} of which the n ranged from 6 to 12 (**4a-4g**). Upon heating the molecules containing n = 8-10 and n = 12 exhibited the endothermic peaks characteristic of the crystal-mesophase transition in addition to crystal-crystal subphases. Tetrasubstituted symmetrical benzidine oligomers compounds with odd number of alkoxy carbon chain possess lower curing temperatures in comparison with their members with even parity. In both odd and even analogous compounds, the curing temperatures decreased upon the increase of n. The optimization of geometric structures together with the global hardness η (in eV), global softness S (in eV^{-1}), electronegativity χ (in eV), and dipole moment (DM, in Debye) of multi-arm molecule with variable terminal carbon chain lengths were evaluated also using the Gaussian calculation at ωB97X-D/6-311+G(d,p) and ωB97X-D/6-31G(d) levels. Based on the calculation, the four identical arms were stabilized by the intramolecular hydrogen bonding. However, the alkoxy chains length have not affected HOMO-LUMO at the optimized molecular geometry.

CHAPTER 1

INTRODUCTION

1.1 State of matter

Matter is described as any substance that occupies space and has mass as well as exists in different stable states relying on the volume, temperature, and pressure of the surrounding. The most fundamental states of matter of solid, liquid, and gas (Eliezer et al., 2001). Generally, the distinction among the state of matter is based on the particle arrangement in different geometrical configuration under different thermodynamic conditions (Rizvi, 2003). In solid state, the particles are packed closely together, therefore, cannot be compressed easily. Solid has a rigid shape and volume. This is due to the strong intermolecular forces acting on the molecules that make the molecules unable to move freely but only vibrate and rotate at a fixed position and orientation. In the liquid state, the molecules are closely packed together but with no fixed arrangement. Therefore, they can vibrate, move freely, slide over each other and able to fill the shape of containers (Tabor, 1991). Liquid is much easier to compress in comparison to solid. Whilst in the gas state, they are highly compressible because of widely spaced molecules having sufficient empty space among them. The molecules are very apart in a random manner. Hence, the intermolecular interaction between their molecules is negligible.

In addition, the wide range of materials in the state of matter that cannot be classified merely as simple liquid or crystalline solids, commonly referred to soft condensed material which is also known as soft matter or complex fluid (Jones, 2002).

1.2 Soft condensed materials

As its name implies, soft matter deals with materials that are easily deformed. Soft matter has intrinsically heterogeneous structure, with complex interactions across different length scales and slow dynamics. The subtle interplay between interaction and thermal fluctuations can lead to complex emergent behaviour, such as spontaneous pattern formation, self-assembly, and large response to small external stimuli (Van Der Gucht, 2018). Soft materials are important in a wide range of technological applications. They appear as packaging materials, foams and adhesives, detergent, cosmetic, paints, food additives, lubricants, and rubber. These materials, which include polymers, gels, colloids, emulsions, foams, surfactant assemblies, liquid crystals, granular materials, and many biological materials, have in common that they are organized on mesoscopic length scales, with structural features that are much larger than an atom, but much smaller than the overall size of the materials (Dshemuchadse et al., 2021; Kim et al., 2017; Schulze et al., 2017; Lee et al., 2014; Fischer et al., 2011; Peterca & Percec, 2010; Engel & Trebin, 2008). The larger size of the basic structural units and the relatively weak interactions that hold them together are responsible for the characteristic softness of these materials (Nagel, 2017).

In more precise terms, the soft condensed materials we are focusing on this thesis include the unique state of matter which is liquid crystal, where it is referred as substance that shows the intermediate state, called mesophase which exists between crystalline solid and isotropic liquid (An et al., 2016; Mohanty, 2003). Liquid crystal also exhibits a responsivity to electric fields that makes them very important as materials in display devices (LCDs) (Scutaru et al., 2019).

1.3 A general overview of liquid crystal

The term "liquid crystal" (LC) refers to an aggregation state that falls in between crystalline solid and amorphous liquid. The molecules in a normal liquid have enough thermal energy to overcome the intermolecular interactions and move about freely. Isotropic describes the arrangement of molecules in a liquid as being equally disorder in all directions. However, because LCs are anisotropic, their characteristics vary depending on the angle at which they are seen. Consequently, due to the degree of alignment of the molecules, LCs are not as disorganised as liquid (Singh et al., 2012; Takezoe & Eremin, 2017). Figure 1.1 shows the molecular orientation between the crystalline solid, liquid crystal, and isotropic liquid.

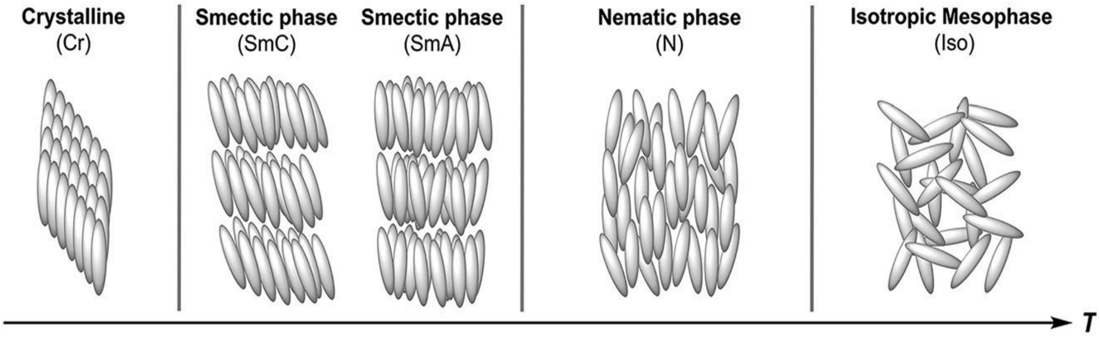


Figure 1.1. Molecular arrangement in a) crystalline, b) LC state: smectic C (SmC), smectic A (SmA), nematic (N), and c) isotropic (I) (Hähsler et al., 2020).

A typical LC molecule may be broken down by two components: i) the central rigid part, and ii) the flexible side chain. The intense intermolecular interaction causes the LC molecules to position themselves preferentially parallel to one another. The characteristic feature of LC is the presence of long-range orientational order in the arrangement of constituent molecules, and sometimes one- or two- and even three dimensional long-range translational or positional order. LCs display a wide range of phases that differ from one another in terms of physical characteristics as a crystalline solid and an isotropic liquid. They display particularly distinct electro-optical phenomena that neither solid nor liquids can match (An et al., 2016).

The physical properties of LC medium are governed by the orientational order of the constituent anisotropic molecules. The orientation of LC molecules could be effectively monitored by weak electric or magnetic fields owing to their isotropic nature. It is possible to change the resultant optical and mechanical properties of the medium by changing the LC molecules orientation. All these factors are important for the functioning of LC display devices such as digital watches, calculators, panel TVs and thermometer (Chandrasekhar, 1992; Demus et al., 1998; Demus et al., 2008; Gray et al., 2009; Demus et al., 2011; de Gennes & Prost, 1995; Collings & Hird, 1997; Kumar, 2001).

1.4 Problem statements

Schiff base liquid crystal have been given special attention since years ago as they provide rigid core structure and enhance mesophase formation by preserving linear geometry, higher stability and polarity or imine linkage (Chiou et al., 2016). However, there are several drawbacks found in the previously reported liquid crystal materials comprising Schiff base as the one of the mesogenic group connected to a rigid core system where their drawbacks have drawn our interest to redesign the molecular structure that led to significant progress. Day by day, the excitement of the researchers to diversify the molecular design in studying the liquid crystalline behaviour is growing. The synthetic studies have led to significant progress in the design of the bent shaped LCs as they exhibit a wide range of mesomorphic behaviour (Pelzl et al., 1999; Takezoe & Eremin, 2017). However, the majority of existing research focussed on the bent shaped LCs structures are 1,3-disubstituted benzene derivatives (Ros et al., 2005). The disclosure on the influence of molecule with the mesogenic segments attached to a benzene ring in the 1,2-positions and their mesomorphic properties relationship remains scarce. From the previous study, the bent shaped molecules with small bending angle are known to exhibit mesophase similar to those shown by classical rod-like shaped (Eichhorn et al., 2002). It is well established that the mesomorphic behaviour of these two types bent shaped molecules are different and this may be attributed to the angle between mesogenic segments attached to the central benzene nucleus (Ting et al., 2020; Yelamaggad et al., 2004). Therefore, in the present study, in order to understand the underlying structure properties relationship further, the bent-shaped compound with two Schiff base mesogenic arms attached directly to a phenyl core at 1,2- position will be introduced and the mesomorphic behaviour of synthesized compound will be investigated. The other shortcoming which was found to be very rare in earlier reported non-conventional liquid crystals with Schiff base moiety was the absence of the hydroxyl group (Yelamaggad et al., 2004). It is notable that the presence of azomethine group (C=N) and OH group shows strong hydrogen bonding interaction, which induce and stabilize the mesophase (Chiou et al., 2006; Pajak et al., 2001). Hence, the structural modification of bent-shaped and multi-arm molecules will be employed in this research by introducing hydroxyl group along with two and four identical mesogenic units possessing imine (C=N) and ester (COO), respectively.

1.5 Research objectives

The objectives of this research are as follow:

(a) To synthesize non-conventional LC (V-shaped and multi arm) compounds with minimal angle bending by introducing different numbers of Schiff base and hydroxy group.

(b) To characterize and investigate the liquid crystalline behaviour of V-shaped and multi-arm liquid crystal by CHN analysis, FT-IR and NMR along with thermal and optical analysis, respectively.

(c) To elucidate the influence of different number of carbon atoms at terminal alkoxy chains on the thermal and optical behaviours of non-conventional bent-shaped and multi arm liquid crystal molecule.

1.6 Research scope

The research work in this thesis involves the study of bent-shaped and multi arm liquid crystal compounds with small or minimal angle bending on the spectroscopic analysis, and liquid crystalline properties. These compounds consist of imine (C=N) and hydroxy (OH) group with the terminal alkoxy chain n = 6-12. The present work focusses on the synthesis the liquid crystalline compounds in which the alkyl chain varied from n= 6 to n = 12 since it is the optimum conditions to observe the mesomorphic properties (Al-Mutabagani et al., 2021; Alamro et al., 2021). It is said that the terminal flexibility has a big role in the thermal stability of liquid crystal phase as the terminal alkoxy chain length of the molecule increase, the rigidity of the central part will be decreased. So, the linearity of the molecule slightly decreases due to the greater number of configurations of the terminal chains which leads to the strong terminal interaction and hence it lowers the phase transition temperature of mesophase

(Altowyan et al., 2021). The evaluation on the effect of different terminal alkoxy chain and the influence of OH group on the liquid crystalline behaviour will be investigated in the present work. Moreover, this research also covers the density functional theory (DFT) calculation on the multi arm molecule. The DFT calculation on the multi arm molecule is chosen as the representative in this work since the compound is more complicated in design and contain similar mesogenic groups with bent shaped molecule.

In general, the V-shaped compounds presented in the first series made up by a central phenyl core attached by diimine with extended side arm consists of ester (COO) groups along with different terminal alkoxy chain $-OC_nH_{2n+1}$ (n = 6-12). While the second series which is multi arm molecules consists of biphenyl core derived from 3,3’-diaminobenzidine which is connected by four side arms of imine moieties. Both series possess OH group in the *ortho*-position. The side arms connected to the central core are identical and positioned next to each other with a minimal distance equivalent to an aromatic C=C bond. The molecular structures for the synthesized compounds were elucidated using CHN microanalysis and various spectroscopic techniques such as fourier transform infrared (FT-IR), and nuclear magnetic resonance (NMR). The texture of LCs was observed by polarizing optical microscopy (POM). Differential scanning calorimetry (DSC) was used to determine the phase transition temperatures and associated enthalpy values of the synthesized compounds. The density functional theory (DFT) for multi arm compound was investigated by Gaussian 16 aiming at establishing the connectivity between the chemical reactivity and fluidity of these target molecules containing different alkyl chain length.

CHAPTER 2

LITERATURE REVIEW

2.1 History and development of LCs

Friedrich Reinitzer, an Austrian botanist, made the first discovery of LCs in 1888. He discovered that the carrot-extracted cholestryl benzoate exhibits two unique phase transition temperatures. He observed that at a temperature of 145.5 °C, the white, fine cholestryl benzoate melted into a hazy fluid. He initially believed that the reported compound’s turbidity was caused by the presence of impurities, but further research disproved this theory. On further heating, the cloudiness suddenly faded and became a clear transparent liquid at 179.0 °C (Kawamoto, 2002). He also notices that blue and violet colours briefly appeared before disappearing with the sample, leaving a lactescent fluid that was turbid yet fluid. The sample recrystallized after the continual cooling revealed the reformation of the violet and blue colours. A detail study of this phenomenon was conducted in 1889 by German scientist, Otto Lehmann. He discovered the optical anisotropy of the opaque phase exhibited a double refraction effect, a characteristic of crystal in Reinetzer’s sample. Afterward, he started referring to this mesomorphic condition as “fliessende krystalle”, also known as LC (Kawamoto, 2002; Mitov, 2014).

Ludwig Gatterman and co-worker produced the initial synthetic LC of *p*-azoxyanisole in 1889. Based on their structural characteristics, A French mineralogist, Georges Friedel developed a classification of LC (nematic, smectic and cholesteric), and mentioned how the magnetic and electrical fields have an orienting effect (Castellano, 2005). Daniel Voländer investigated the association between molecular architectures and the existence of the liquid crystalline state (Demus, 2001). Pierre-

Golles de Genned, who was awarded with the Noble Prize in Physics 1991, revealed the ordering of molecules in LCs and polymers. He also observed the relations between LCs and superconductors in addition to the magnetic materials (de Gennes, 1972; de Gennes 1992).

2.2 Types of liquid crystal

Thermotropic and lyotropic are two main categories that make up this classification. These types are further distinguished into different phases depending on the modifications in their orientational or positional order caused by variations in external factors such as temperature.

2.2.1 Lyotropic LCs

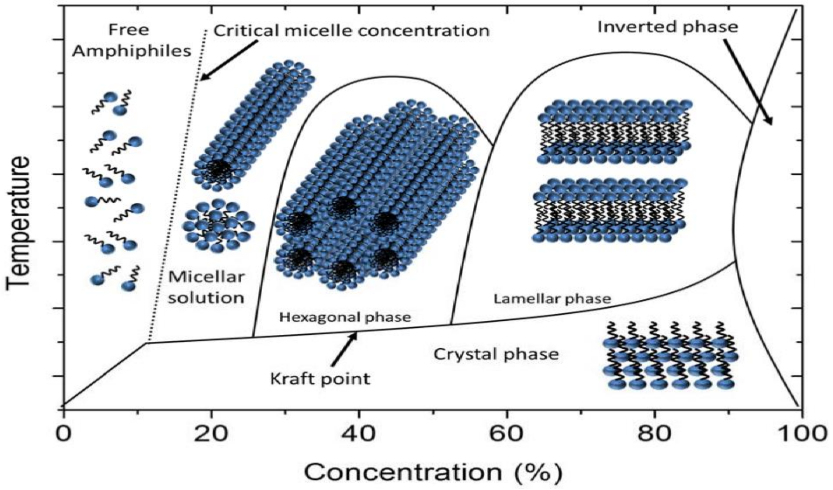


Figure 2.1 Schematic illustration of the phase diagram of an amphiphilic surfactant in an isotropic solvent, forming lyotropic phases (Dierking & Al-Zangana, 2017).

Lyotropic LCs are composed of two or more components where the mesophases are affected by a certain concentration range in the isotropic solvent on the amphiphilic compounds. Typically, molecules are composed of two distinct hydrophobic tail (ionic or non-ionic) groups. In lyotropic phases, the space of the compounds are surrounded by the solvent molecules which contribute to the fluidity of the system (Jameson et al., 2007). The molecules behave independently and the orientation of the molecules is randomly distributed throughout the water or other solvents when the critical micelle concentration (cmc) is reached. As the concentration increases, the size of micelles molecules will be increased leading to the LCs formation, namely the hexagonal and lamellar phase (Barzic & Ioan, 2016; Zhou, 2017; Dierking & Al-Zangana, 2017).

2.2.2 Thermotropic LCs

Thermotropic LCs are single component systems that exhibit liquid crystalline behaviour within a certain temperature range. Melting point is the transition temperature at which crystalline solid (Cr) changed into the mesophase, whereas clearing point in the transition temperature at which the LC phase converted into an isotropic liquid. Thermodynamically stable mesophase which formed upon both heating and cooling cycles are documented as enantiotropic phase whereas the thermotropic mesophase that can only be observed during cooling or heating is termed as monotropic LC. Thermotropic LCs can be classified into two general groups based on the molecular shape of constituent molecules which are conventional LC and non-conventional LC (Ooi et al., 2014). The compound that produce thermotropic LCs often have a hard core (aromatic and non-aromatic) and flexible terminal moiety (aliphatic chain). Mesomorphic characteristics are greatly enhanced by the addition of flexibel terminal chains to the rigid unit. Due to anisotropic dispersion forces and stacking interaction between the molecules, the thermotropic LCs were produced (Gopal Rai et al., 2010).

2.3 The influence of chemical moieties on LCs

The selection of core system, linking (connecting) groups, and terminal moieties, which will be explored in further detail in the next sections, is usually required for the creation of compounds with liquid crystalline behaviour.

2.3.1 Core system

The rigid fragments that are linearly and directly coupled to the aromatic rings, or sometimes joined by a connecting group, are referred to as the core system. The benzene ring, biphenyl, cholesteryl, heterocyclic, naphthalene, thiophene, and alicyclic ring are the most common components of the rigid core units. Maged A. Osman investigated how the hard core of the molecules structural variations affected the characteristics of the LCs in 1983. Osman discovered that the attractive interactions (Van Der Waal's forces) between the LC molecules, especially the dispersion forces of electrons localized in σ-bonds, provide the background necessary to sustain the liquid density. He also added that the strength of the molecular interactions which is quite sensitive to the intermolecular separation influences the thermodynamic stability of the mesophase. Although the orientation dependent energy is required to account for the thermotropic phase transition, the steric factors play the predominant role since they govern the packing and consequently the intermolecular separation. Interaction between the alkyl chains as well as their conformational isomerism influence the stability of the mesophase (Osman, 1983). It has been comprehensively demonstrated that increasing the number of aromatic rings in the LCs compound core structure and lengthening the hydrocarbon chains had a significant impact on the mesomorphic behaviour and transition temperature (Fornasieri et al., 2003).

2.3.2 Linking group

There are several functional groups that have been employed as connecting groups (common example: -CH=N-, -N=N-, -COO-, -CH=CH-, -CH_2-CH_2-, and -C≡C-) between two or more aromatic rings, where the presence of the connecting groups helps to preserve the molecular linearity and boost the polarizability anisotropy. As a result, it offers great molecular length stability and permits the creation of mesophases (Collings & Hird, 1997). Jankowiak et al. (2009) studied at how the connecting group affected the behaviour of different series of isostructural compounds made up of *p*-carborane derivatives and their hydrocarbon equivalents. The study demonstrated that the effectiveness of the connecting group in mesophase stabilization follows the order of -CH_2-CH_2 < -COO < -OCH_2 < -OCC in *p*-carborane derivatives and their hydrocarbon counterparts. They also observed that the -CH_2-CH_2- and -OOC- connecting groups of *p*-carborane derivatives destabilized the mesophase more than those of carbocyclic derivatives.

2.3.3 Terminal moieties

The introduction of the terminal moiety is necessary to balance the molecular structure and produce the mesophases because the rigid core alone has a significant tendency to not exhibit any LCs properties. A surprising range of terminal substituents, including polar terminal substituents and flexible terminal chains (alkoxy and alkyl) has been implemented in molecular design of a compound to exhibit the LCs properties. Jber et al. (2014) investigated the influence of various terminal alkoxy chains, C_nH_{2n+1} (n = 1-8), of the Schiff base esters, and found that the mesomorphic behaviour was significantly affected by the lengthening of the terminal alkoxy chain. Throughout their investigation, they discovered that monomers with short terminal alkoxy chains (n = 1 and n = 2) lack LCs characteristics due to molecular stiffness, resulting in a high melting point and preventing their mesomorphic behaviour. Increasing the number of carbon atoms in the terminal alkoxy chain from n = 7 to n = 8 suppressed the presence of N phase and led to the creation of Sm phase. The molecule axis can be stabilised by strong intermolecular interactions owing to the polar terminal groups (Ooi et al., 2013). In another study, the impact of terminal non-polar (alkyl and alkoxy) substituents on the thermodynamic mesophase stability in relation to their impact on molecular packing was investigated. It is shown that, there is an increase of clearing point with increasing chain length in series with low nematic to isotropic (N-I) transitions, while those with high clearing points either remain steady or suffer a decrease in their N-I transition on going to the higher homologues. These phenomena have been related to changes in the anisotropy of polarizability with increasing chain length (Osman, 1983).

2.4 Geometrical shapes of thermotropic LCs

Geometrical shapes of thermotropic LCs can be divided into two categories: i) conventional LCs, and ii) non-conventional LCs.

2.4.1 Conventional LCs

Among the thermotrpic liquid crystals, rod-like and disc-like molecules are generally consider as conventional liquid crystals.

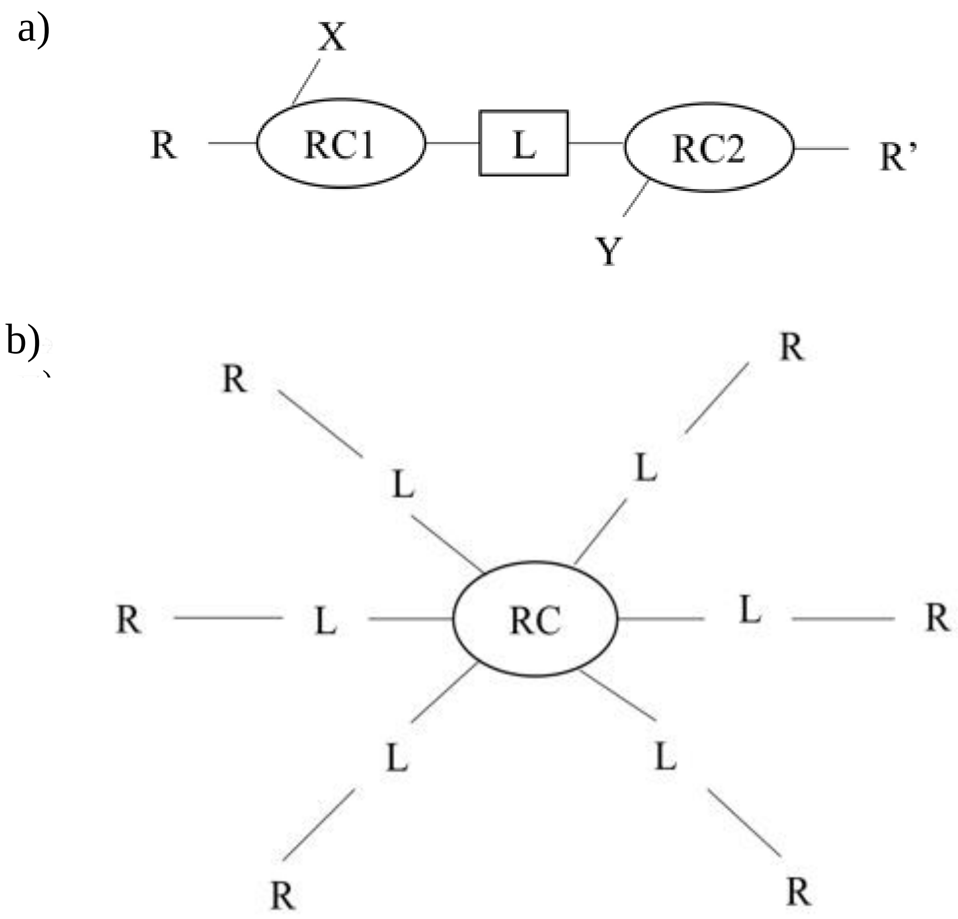


Figure 2.2 General templates for the a) rod-like and b) disc-like shaped liquid crystals.

For many years it was believed that the molecules that exhibited liquid crystal molecules has to be long or rod-shaped (Volander, 1908). However, Chandrasekar et al. (1977) demonstarted that disk-like molecules display mesomorphism. RC, RC1 and RC2 are rigid cores that are often aromatic in nature but can also be alicyclic. In many examples these two cores are connected via a covalent bond and in some cases they are connected by linking unit L (-COO-, -CH_2-CH_2, -CH=N-, and -N=N-). the terminal substituents R and R’ are usually either alkyl or alkoxy chains. In many cases one of the terminal units is polar substituent (CN, F, CNO, NCS, and NO_2). In some special cases the lateral units X and Y (F, Cl, CN, and CH_3) are incorporated in the main molecular structure (Yu & Saupe, 1980). By employing rod-like mesogenic segments, two types of liquid crystalline polymers (LCPs) have been reported (Chandrasekhar et al., 1977). They are main chain and side chain LCPs. Main chain LCPs consist of rod-like anisotropic repeating units that form a long chain. In side chain LCPs, rod-like mosgenic units are attached to the side of the polymer backbone. Inclusion of molecular chirality in rod like molecules furnishes chiral liquid crystal and is known to exhibit various chiral structures (Kitzerow & Bahr, 2001).

2.4.2 Non-conventional LCs

With the evolution of liquid crystal science and technology, non-conventional LCs continue to captivate researchers. Non-conventional LCs are created via a self-assembly mechanism including covalent complex molecules connecting numerous mesogenic (anisometric) segments through discrete molecular fragments, such as chains or spacers. Numerous studies have shown that the anisotropic non-covalent LC molecules shapes significantly affect the mesomorphic behaviour in which the molecules support liquid crystallinity (Ooi et al., 2013). These LCs molecules are compensated by the nano-segregation of physically or chemically incompatible molecular fragments and the propensity towards the efficient space filling in the condensed matter (Skoulios et al., 1988; Pegenau, 1999; Tschierke et al., 2001; Achalkumar et al., 2011). Some non-conventional LCs are oligomers, dimers, dendrimers, dendrons, bent-core molecules, multi-armed mesogens, rod coil molecules, metallomesogens, and hydrogen-bonded mesogens (Zhang, 2008; Ooi et al., 2013; Gupta et al., 2013; Pathak et al., 2016).

2.4.2(a) Bent-shaped LCs

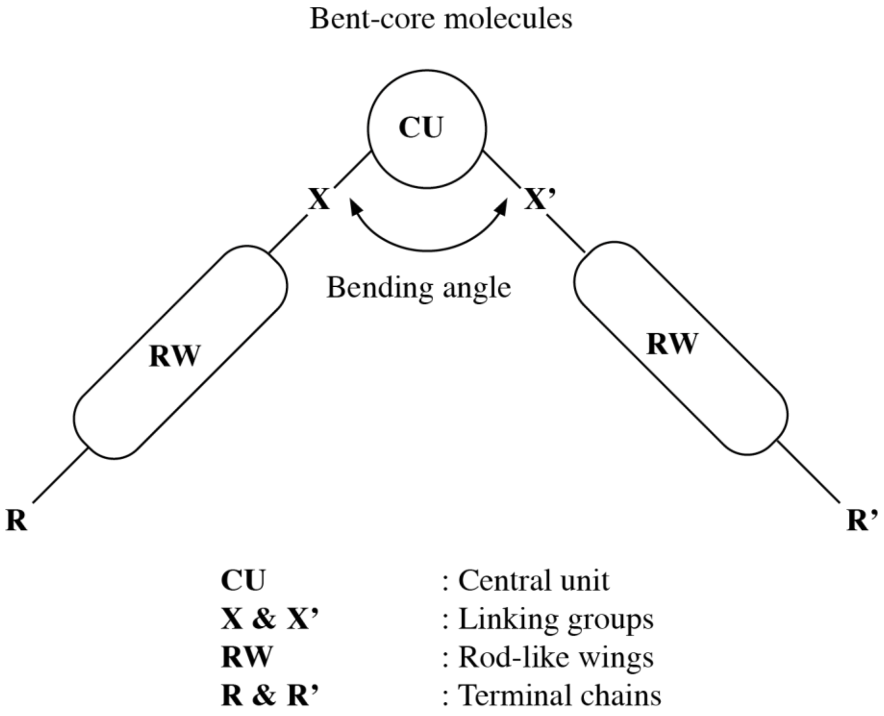


Figure 2.3 General template of bent-core molecules.

The first mesogens were synthesized by Vorländer in the beginning of the twentieth century. Vorländer synthesized more than 2000 mesogenic compounds including mesogenic dimers with flexible spacer, metallomesogens, main-chain polymers, ferroelectric chiral SmC, and columnar mesogens. Among them the bent-core mesogens wherein a central aromatic core linking two-ring mesogenic units in the *o*- or *m*-positions were included (Pelzl et al., 2001). Thus, Vorländer is believed to be the pioneer in this area who synthesized bent-core liquid crystals. However, Vorländer also mentioned that the thermal stability of these mesogens is low as compared to the rod-shaped analogs, and the liquid crystalline state is obtainable by an utmost linear shape of the molecules but not by a non-linear shape.

The first synthesis of bent-core mesogens by Voländer remained unnoticed. Matsunaga et al. (1993) started to systematically synthesize bent-core molecules.

Matsunaga's group was interested in examining the incompatibility of non-linear molecules with liquid crystallinity but not in studying their physical properties. They first synthesized 1,2-phenylenebis[4-(4-alkoxybenzylideneamino)benzoates] particularly with long alkoxy end chains, which were not synthesized by Vorländer. They found the nematic (N) phase in the homologues with the shorter chain lengths, the smectic A (SmA) phase in those with longer chain lengths, and both N and SmA phase in those with middle chain lengths (Kuboshita et al., 1991; Matsuzaki & Matsunaga, 1993). They also examined the phase behaviour by the substitution of the central aromatic ring. Then, they extended their systematic works of bent-core molecules with an acute-angled configuration to those with an obtuse-angle configuration. Akutagawa et al. (1994) identified two mesogenic phases, SmC, and more ordered Sm phases in the compound. At the same period, Janietz et al. (1993) examined the liquid crystallinity of bent-core molecules containing a 1,3,5-triazine central core with a 6-alkoxy unit. They reported the existence of the N phase in most of the homologues. A Sm phase also emerged in one of the homologues with a 6-methyloxy in the central core and long terminal chains.

Bent-shaped mesogens are strongly anisometric molecules. Their rotation around their mean long axes may be strongly hindered. This means that an uniaxial cylinder shape model adopted for rod-shaped mesogens cannot be applied for bent-shaped molecular systems. The N phase formed by bent-shaped mesogens seems to be the same as the conventional N phase consisting of rod-shaped molecules. Well-known physical phenomena such as flexoelectric effect and electroconvection have been observed in the "banana" N phase too. Orientational elasticity and formation of the blue phases occur in the bent-core nematic. However, these phenomena are quantitatively and sometimes even qualitatively quite unique in bent-shaped molecules (Takezoe & Eremin, 2017).

2.4.2(b) Multi-arm LCs

Multi-arm LCs with unconventional mesogens are a type of molecules constructed from multifunctional cores and linear mesogenic or pro mesogenic arms attached, displaying N, Sm, cubic, and columnar liquid crystalline phases (Wang et al., 2019). The mesophase of multi-arm LCs are not only similar to the rod-like molecule N phase but also similar to disc-like LC columnar phase, which is the bridge that connects rod-shaped and disc-like LC, while it is the foundation of the dendritic LC macromolecule (Brostow & Jaklewicz, 2004; Kohout et al., 2010). In short, the multi-arm LC attract more interest in research with its unique structure and performance. Some multi-arm LCs with almost the same mesogenic arm introduced look like a star in structure, which used to be called star-shaped. In 1988, Chandrasekha synthesized the star LC molecules which the central part of which was a copper atom, and the connected way of LC element was a coordination bond. Such compounds showed that biaxial nematic phase could be regarded as the combination of rod-like and disc-like elements, and its phase behaviour was uncommon (Tian et al., 2010). The star-shaped LC molecules was synthesised by Attard et al. (1992), which centre was trimesic acid, flexible linker was hexylene glycol, and LC nuclei was Schiff base mesogen. It showed the Sm and N phases, which was due to the presence of longer flexible linking groups. As such, the molecules were arranged in nearly parallel state in the LC substrate. The N and Sm phases thus formed possess the same behaviour as the LC phase associated with the rod-like molecule (Attard et al., 1992). Zhou synthesized the star shaped LC which had a core of silicon atom, and the connectivity among the LC component was the covalent bond. When this type of compound transforms to the LC phase, it appeared the pattern and filamentary texture of typical N phase (Zhou et al., 2017). In addition, the star-shaped LC molecules having the characteristic of the disc-like LC phase also had been designed and synthesized.

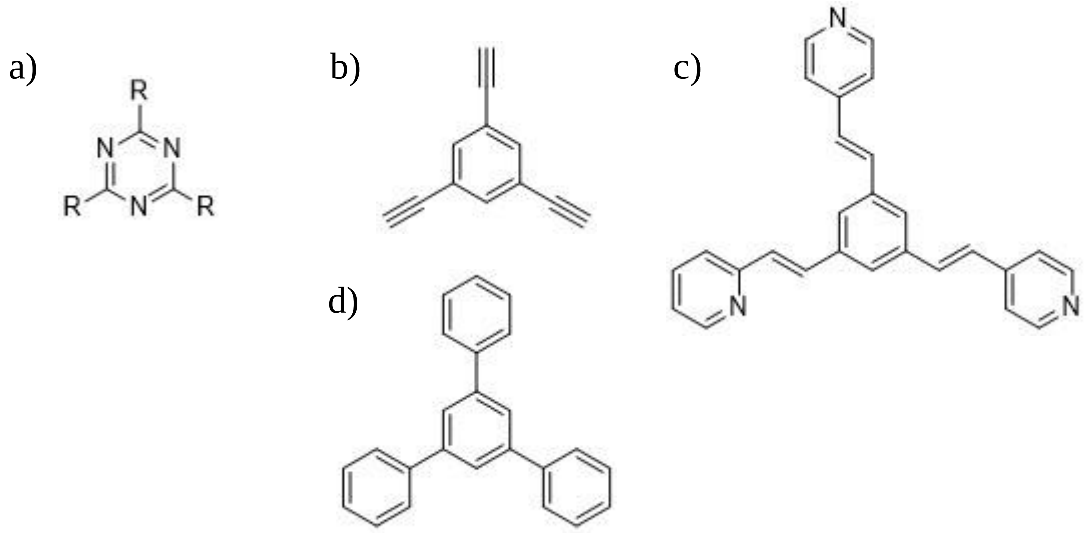


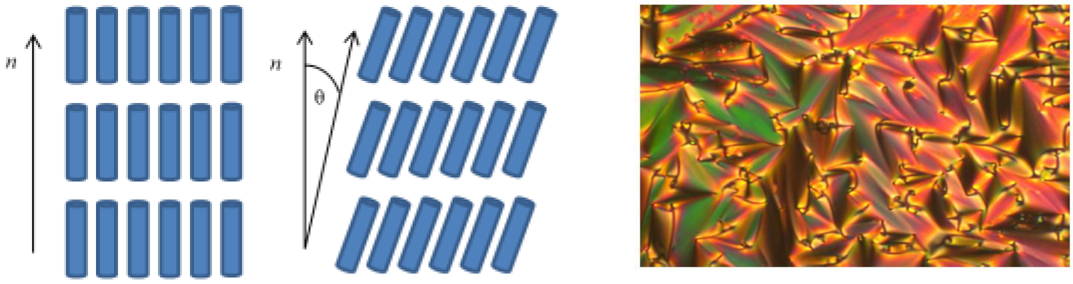
Figure 2.4 a) Triazine, b) triethynyl benzene, and c) tristyrylpyridine core reported by Jhun et al. (2012) and d) triphenylbenzene core reported by and Obsive et al. (2018).

The compounds with external rigid LC arms were reported successively in which the centers were triazine, triethynylbenzene, tristyrylpyridine and metallic copper, nickel, palladium and so on, and they showed a disc-like columnar phase (Jhun et al., 2012). Olate et al. (2017) designed a novel luminescent star-shaped LC molecule in 2016 with various terminal alkyl chain length from n = 10-14. The molecule with n = 12 display an enantiotropic hexagonal columnar mesophase while the other molecules did not exhibit any mesomorphic properties. They also highlighted that the mesomorphism is the result of a subtle balance between the flexible peripheral hydrocarbon region and the rigid inner core (Olate et al., 2017). Eremin et al. (2018) developed dendrimers with azo-containing periphery as photoactive interfaces for LC systems. All dendrimers exhibited smectic (mostly SmA) LC phases (Eremin et al., 2018). Obsiye et al. synthesized a series of dendrimers consisting of star-shaped triphenylbenzene core unit and bulky lateral groups. All dendrimer derivatives is reported to exhibited enantiotropic columnar hexagonal mesophases (Obsive et al., 2018).

2.5 Mesophase of LCs

2.5.1 Smectic phase

Daniel Voländer made the first discovery of the mesomorphic behaviour of the smectic (Sm) phase in 1908. (Demus, 2001). In compared to the nematic LCs, the Sm phase has been thought to be a more complicated and organised phase in arrangement. The Sm phases exhibit orientational order and have a greater level of positional order than the nematogenic phase. As compared to nematic LCs, Sm LCs occur at lower temperature ranges. As a result, the molecules are able to arrange themselves into clearly defined layers that may slide against one another and be seen like layers of soap (Kelker & Hatz, 1980). Smectic A (SmA) and smectic C (SmC) phases may be distinguished from one another based on packing formation and layer system order.



a) b) c)

Figure 2.5 Illustration of the a) molecular arrangement of SmA, b) molecular arrangement of SmC (Carlescu, 2019), and example of SmA phase c) focal conic fan texture (Cook et al., 2012).

The molecules in the SmA phase has been acknowledged as the least order among all types of Sm phases wherein the molecules are parallel to each other and they are organized in the diffuse layers with the orientation of the long axes perpendicular to the layer plane. Consequently, the Sm phase fluidity characteristics are significantly more viscous than those of the nematic phase. This phenomena may be explained by the high lateral forces between molecules and the weak interlayer interactions that enable the molecules to slip effortlessly past one another (Chandrasekhar, 1983; Chandrasekhar, 1992).

Similar to the SmA phase, where the molecules are parallel to one another, the molecules in the SmC phase have a similar molecular distribution. In contrast to SmA phase, the long axes of SmC phase are tilted at an angle (θ) with regard to the layer planes instead of being perpendicular to the normal layer. If both phases are present in a comparable molecule, the SmC phase will often occur at lower temperatures than the SmA phase (Pershan, 1988).

2.5.2 Nematic phase

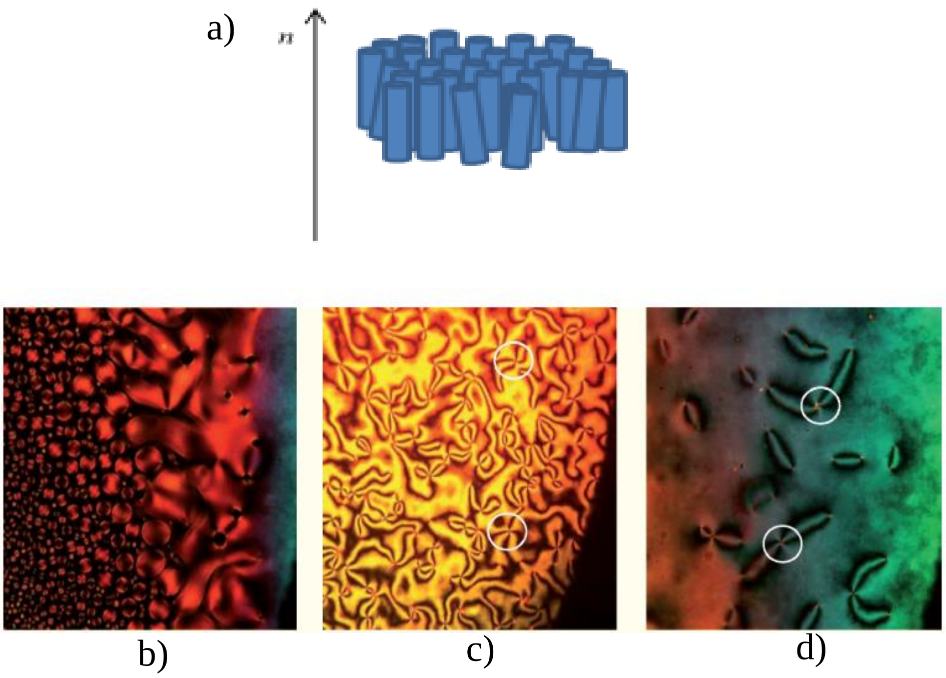


Figure 2.6 Illustration of the a) molecular arrangement of nematic phase, example of nematic phase texture b) nematic droplets, c) schlieren texture of four-brush disclinations, and d) schlieren texture of two-brush disclinations (Carlescu, 2019).

Nematic phase has been discovered as the most disorganised mesophase with the greatest degree of symmetry which is most similar to the isotropic liquid state. In order to achieve spontaneous long-range directional order, the molecules self-align in the same direction, known as director, *n*. Therefore, there is no positional order to the molecules, and the center of molecular phases are spread out randomly (Carlescu, 2019).

2.5.3. Discotic nematic phase

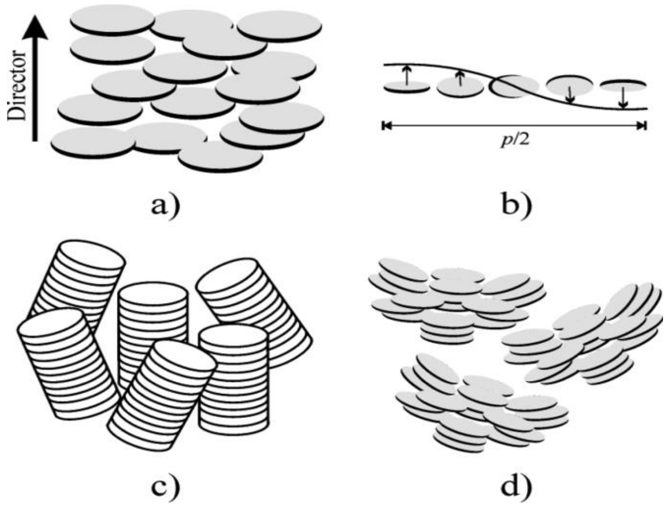


Figure 2.7 Different nematic phases of discotic liquid crystals: a) discotic nematic N_D, b) cholesteric N_D*, c) columnar nematic Nc, and d) lateral nematic N_L phase (Bisoyi & Kumar, 2010).

Nematic phases are the simplest liquid crystalline phases formed since they only have long-range orientational order (of molecules, columns, etc.) and no degree of long-range translational order. For discotic molecules, different kinds of nematic phases are known (Figure 2.7). In a discotic nematic mesophase (N_D) the nematic phase is built of single flat molecules which possess full translational and orientational freedom around their principal short axes. Their long axes, however, are on average oriented parallel to a general plane (Figure 2.7a). In contrast to the rather waxy columnar phases the nematic phases are fluid. There is also a chiral variant of the discotic nematic phase known, the cholesteric phase (N_D*) (Figure 2.7b), which is formed by chiral discotic mesogens or after the addition of a chiral dopant to an achiral discotic nematic phase. It exhibits a twisted nematic structure where the director field is continuously twisted in the direction normal to the local directors *n*(r) (Figure 2.7b) with the pitch of the helical structure (Wöhrle et al., 2016).

The columnar nematic mesophase (Nc) is formed out of columns as building blocks (Figure 2.7c). An example is the case of an electron donor doped with an electron acceptor (Praefcke et al., 1991; Praefcke et al., 1992). In this respect, the ordered columns are built owing to the existence of charge-transfer interactions. The formation of a 2D-lattice is prevented by the molecules with strongly differing lengths of their side chains.

Besides these two nematic phases, the lateral nematic phase ($N_{L)}$ was also observed (Bisoyi & Kumar, 2010). The lateral nematic phase is built of aggregates formed by multiple discotic mesogens. These supramolecular aggregates then organize into a nematic phase (Figure 2.7d).

The biaxial nematic phase is an optically biaxial nematic phase where the long-range orientational order is not only found in one direction but also in two additional mutually perpendicular directions (Mederos, 2014). These biaxial nematic phases are known for quite some time in lyotropic (Yu & Saupe, 1980), polymeric (Hessel & Finkelmann, 1986) and more recently in mineral liquid crystals (Van den Pol & Petukhov, 2009). In the case of discotic LCs, the formation of a biaxial nematic phase is expected in mixtures of rod- and disc-like mesogens (Tschierske & Photinos, 2010).

2.6 Density functional theory (DFT)

Throughout the years, the correlation between LCs and density functional theories (DFTs) calculation has attracted various researchers due to their beneficial potential in the technological development and scientific areas. DFTs are capable of predicting the phase diagram of LCs, including orientational or translational ordered phases such as N and Sm, and describing a structure near a solid surface (Avazpour & Avazpour, 2010). DFTs allow to minimize, optimize, and include the estimation of the structural optimization for each compound to find the minimum energy geometrical structure. The optimization process has been carried out to find the geometrical structure for the minimum energy of conformations, whereas the atoms, the bond length, and the bond angle of the compounds modified until a new minimum energy geometrical structure is established. The optimized structured were used in the estimation of the frequency as well as many important thermodynamic parameters (Mohammady et al., 2021).