Steric Interaction and Phase Behavior of Some Laterally Substituted Liquid Crystalline Compounds

Submitted for
Partial Fulfillment of the Requirements of
M.Sc. in Chemistry

By
Hoda Abd Elrazik Ahmed
B.Sc. in Chemistry

Department of Chemistry
Faculty of Science
Cairo University

2009

Cairo University
Faculty of Science

TO WHOM IT MAY CONCERN

This is to certify that Hoda Abd Elrazik Ahmed has attended and passed the following post graduate courses as a partial fulfillment of the requirements of the degree of master science.

1- Quantum chemistry.
2- Molecular structure.
3- Advanced analytical chemistry.
4- Physical polymers.
5- Adsorption.
6- X-ray diffraction and thermal analyses.
7- Advanced inorganic chemistry.
8- Thermodynamics.
9- Statistical thermodynamics.
10- Molten metallurgy.
11- Nuclear chemistry.
12- Catalysis and colloids.
13- Group theory.
14- Electrochemistry.
15- Electrode kinetics.
16- Mechanisms of inorganic chemistry.
17- Solar energy.
18- Chelatimetry.
19- Volummetry.
20- German language.

This certificate is issued at his own request.

Abstract

Name: Hoda Abd Elrazik Ahmed Ahmed

Title of the thesis: Steric Interaction and Phase Behavior of Some Laterally Substituted Liquid Crystalline Compounds.

Degree: Unpublished M.Sc. Thesis, Faculty of Science, Cairo University, 2009.

Two groups of the compounds, 4-(4'-substituted phenylazo)-2-(or 3-) methyl phenyl-4"-alkoxy benzoates, were prepared and investigated for their mesophase formation and stability. Each group constitutes five homologous series that differ from each other by the terminal small compact substituent. The later varies between CH_3O, CH_3, H, Cl, and NO_2, and within each homologous series, the number of carbons in the alkoxy chain varies between 8, 10, 12, 14, and 16. The difference between the two groups of compounds lies in the orientation protrusion of the laterally- substituted methyl group into the central benzene ring. In the first group (Group **I**) the methyl substituent, introduced into the o-position with respect to the ester group, makes an angle of 60^o with the long axis of the molecule. In the other group of compounds (Group **II**), the orientation angle is 120^o since it is introduced into the m-position. A new type of binary phase diagrams could be constructed, in which the two components are corresponding positional isomers from either group. The study aimed to investigate the effect of inclusion of the lateral methyl group, as well as its spatial orientation, on the mesomorphic properties of the produced derivatives in their pure and mixed states. Molecular formulae of the compounds in both groups were confirmed via elemental analyses, ir, nmr, and mass spectroscopy. The compounds prepared, in both groups, were characterized for their mesophase behavior by differential scanning calorimetry, DSC, and phase identified by polarized light microscopy, PLM. The nematic phase is the only mesophase observed in most of the compounds prepared and their binary mixtures.

Supervisors: 1.prof. Dr. Magdi M.Naoum.

2. Dr. Sayed Z. Mohammady.

Prof.Dr. Mohamed. M. Shokry, Chairman.

Department of Chemistry
Faculty of Science
Cairo University

Acknowledgment

First, I thank **God** for helping me to accomplish this work.

I'd like to express my deep thanks and gratitude to ***Prof. Dr. Magdi M. Naoum.,*** Professor of Physical Chemistry, Department of Chemistry, Cairo University, for his continuous discussion, valuable remarks, encouragement, guidance, and supervision.

Also, I appreciate the efforts made by ***Dr. Sayed Z. Mohammady***, Assistant Professor of Physical Chemistry in the same Department, for his support and encouragement.

Finally, I thank all my colleagues in the Department of Chemistry and all my friends for their care, and love.

Hoda Abd Elrazik Ahmed

CONTENTS

Chapter 1

1. INTRODUCTION TO LIQUID CRYSTALS

One is familiar with gases, liquids and solids. However, in the nineteenth century another state of matter was discovered called the liquid crystal (LC) state. The difference between solid crystals and isotropic liquids is that, the molecules in a solid crystal are ordered, whereas in the isotropic liquid they are not. The order in a crystal is usually both positional and orientational, in that the molecules are constrained to occupy specific sites in the lattice pointing their molecular axes, in specific directions. The molecules in a liquid, on the other hand, diffuse randomly through out the sample with the molecular axes tumbling widely.

Perhaps the most important property that differentiates solids from liquids is flow. Liquids flow and take the shape of container, whereas solids do not and retain their shape. The optical properties of liquids and some solid crystals are quite different. For example, some crystals change the polarization of light, whereas liquids do not.

Interestingly enough, many phases were found to possess properties of the crystalline and liquid phases, with a degree of order intermediate between the molecularly disordered liquid and the regular structure of a crystal. These phases are grouped together and called "*Liquid Crystals*" since they share properties normally associated with liquids and crystals. The most important property of liquid crystal phases is that the molecules of which have long-range orientational order. This intermediate phase is identified as being a true phase with definite transition temperature and thus is termed "*Mesophase*" which possesses considerable anisotropy that makes them distinct among ordinary liquids thus, liquid-crystalline phases are also known as mesophases (meaning intermediate phase) or mesomorphic phases, and molecules that compose them are known as mesogens. The fact that most of the order of a crystal is lost when it transforms to a liquid crystal is revealed by the value of the heat of transition. Values observed for crystal-isotropic liquid transition are around 250 J/g. However, when a liquid crystal transforms to an isotropic liquid, the heat of transition is much smaller, typically about 5 J/g.

1.1. Types of liquid crystals:

Transitions to the intermediate mesomorphic states may be induced merely by thermal processes (thermotropic mesomorphism) or by the action of some solvents (lyotropic mesomorphism). From this point, liquid crystals may be classified into two distinct categories: *Thermotropic* and *Lyotropic*. The latter behaves mesomorphically as a function of concentration while the former has a definite mesomorphic behavior within a specific temperature range and may exhibit more than one mesophase depending on temperature.

1.1.1. Thermotropic liquid crystal phases:

The mesomorphic and physical properties of thermotropic liquid crystal materials, and ultimately their suitability for applications, are all fundamentally dictated by the chemical structure of the constituent molecules. Before progressing further, several terms and their definitions need to be clarified. The term "*Mesophase Stability*" refers to the upper temperature limit to which the mesophase exists while the term "*Mesophase Range*" means the temperature range over which this specific phase exists. The tendency of many materials to supercool before they recrystallize enables the mesophase to be exhibited as a metastable state below the melting point, and where the mesophase stability is below the melting point the phase is termed "*Monotropic*". In this case, the mesophase appears only from the isotropic melt by cooling. Conversely, where the mesophase stability is higher than the melting point, the phase is termed "*Enantiotropic*", where the mesophase appears both on heating the solid or cooling the isotropic melt.

Thermotropic liquid crystals are generally further distinguished with respect to the molecular shape of the constituent molecules, being called "*calamitic*' for rod-like (i.e, one molecular axis is much longer than the other two) , "*discotic*" for disk-like (i.e, one molecular axis is much smaller than the other two), and "*banana-shaped*" molecules.

1.1.1.1. Calamitic Liquid Crystals:

A common structural feature of calamitic mesogens is a relatively rigid core, often incorporating phenyl and biphenyl groups, and two flexible end groups, often alkyl or alkoxy chains. As depicted in Figure 1.1, calamitic LCs are those in which the molecular length (l) is significantly greater than the molecular breadth (b).

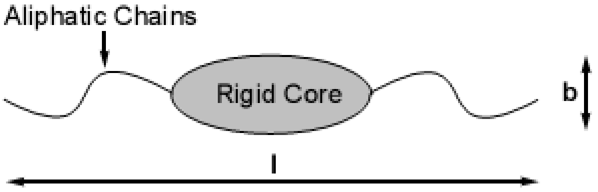

Figure 1.1. Calamitic LCs, where l >> b.

1.1.1.2. Discotic Liquid Crystals:

Similar to the calamitic LCs, discotic liquid crystals possess a general structure comprising a planar (usually aromatic) central rigid core surrounded by a flexible periphery, represented mostly by pendant chains (usually four, six, or eight), as illustrated in the Figure 1.2. As can be seen, the molecular diameter (d) is much greater than the disc thickness (t), imparting the form anisotropy to the molecular structure.

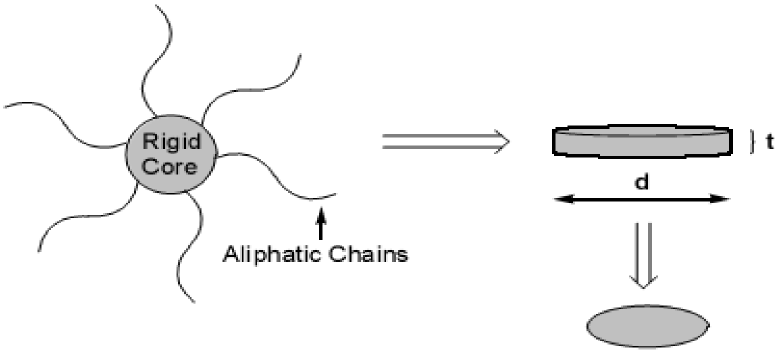

Figure 1.2. The general shape of discotic LCs, where d>>t.

The core of a typical discotic liquid crystal molecule is usually based on benzene, triphenylene, or truxene, with six or eight side chains, each resembling a typical calamitic liquid crystal molecule.

1.1.1.3. Banana -shaped Liquid Crystals:

Banana-shaped mesogens are constituted of two mesogenic groups linked through a rigid group in such a way as not to be co-linear, i.e. bent-core mesogens, Figure 1.3. Both mesogenic groups are mostly calamitic molecules consisting of two aromatic rings with varied linking groups (Y, Y') between them, and a terminal chain in para position with respect to this linking group, on one of the aromatic rings, e.g. 4-(4'-n-octyloxyphenyliminomethyl)- phenylcarbonyloxy fragment. These calamitics are connected to a rigid, mainly six member aromatic ring, so that the angle between the two calamitic wings (α) is around 120°. In case of a benzene ring it means that the mesogens are connected in position 1 and 3, respectively. Thus, the origin of the non-linear shape is the meta-substituted benzene ring.

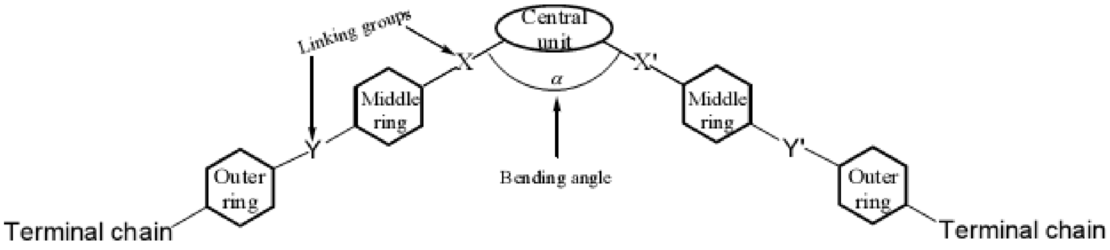

Fig.1.3. General scheme of bent-shaped molecules

1.1.2. Lyotropic liquid crystals:

The action of solvent upon a solid also involves a disruption of the crystal lattice by an attraction of solute molecules from the ordered crystal lattice into the disordered state of solution. The majority of compounds pass quite normally into solution, however, it was observed that, when certain compounds are treated with a solvent they give states which are neither solids nor true solutions, but which are intermediate in character between these two extremes. Such states are in fact *"mesomorphic"* in their properties, and since the effect of the solvent was responsible for their occurrence, the phenomenon is referred to as *"Lyotropic Mesomorphism"* and these compounds are given the name *"Lyotropic Liquid Crystals"*. An excess of solvent will of course cause a lyotropic mesophase to pass over to a true solution, and, on the other hand, evaporation of such a solution will give first the liquid crystalline state before it precipitates the solid.

The recipe of a lyotropic liquid crystal molecule is one that combines a hydrophobic group at one end with a hydrophilic group at the other end. Such amphiphilic molecules form ordered structures in both polar and non-polar solvents. Good examples are the soaps and various phospholipids. When dissolved in a polar solvent, such as water, the hydrophobic tails assemble together and present the hydrophilic heads to the solvent. The resulting structure for soap molecules is called a "*micelle*". If these amphiphilic molecules are mixed with a non-polar solvent such as n-hexane, similar structures are formed but now the polar heads assemble together with the non-polar tail groups are in contact with the solvent. Such phases are called "*reversed phases*" to distinguish them from the phases that occur in polar solvents.

1.2. Calamitic Liquid Crystal Phases:

Calamitic mesogenic (i.e., mesophase-producing) compounds generally consist of long, narrow, lath-like and fairly rigid molecules. In the crystal solid state (Cr) of such compounds, the molecules are held together by strong intermolecular forces of attraction which, due to the rod-like structure, are anisotropic. In simple terms, the smectic phase (Sm) arises if the lateral intermolecular forces of attraction are stronger than the terminal forces. On heating, the terminal forces break down first, in-plane translational order is lost, and this results in a lamellar arrangement of molecules in which the layers are not perfectly defined. Due to possible correlation within and between the layers, there are five true smectic modifications. When the smectic phase is heated, either out-of-plane translational order is lost, which produces the nematic phase (N), or additionally orientational order is lost, which gives the isotropic liquid (I). No single liquid crystalline material exhibits all liquid crystal phase types but many compounds do exhibit two or three types of liquid crystalline phases. In an isotropic liquid (properties are identical regardless of the direction in which they are measured), the constituent molecules are completely disordered with respect to each other; however, they do not possess enough thermal energy to break into the gas phase. In the nematic phase (N), the constituent molecules are also completely disordered with respect to each other, but the long molecular axes statistically point in a preferred direction. This one-degree of ordering of the nematic phase makes it the least ordered liquid crystal phase with a high degree of fluidity. This fluidity, combined with the anisotropic nature of the molecules, is the basis for the operation of liquid crystal displays. The fluid nematic phase has a low viscosity and nematic materials can be designed so that molecular orientation can be switched by an electric field; the different optical properties of the two orientations enables display applications.

The smectic mesophase (Sm) is more ordered than the nematic phase and, furthermore, whereas only one nematic phase exists, the smectic phase exhibits polymorphism, i.e., there are many different types of smectic phases.

Compounds that possess liquid crystalline mesophases can take more than one type of mesomorphic structure, as the temperature is raised [1,2]. Transitions between these various forms occur at definite temperatures. Whereas smectic-smectic and smectic-nematic transitions, in thermotropic liquid crystalline compounds, are known to occur, no nematic-nematic transformations have been observed. It is apparent that for a compound that displays smectic and nematic phases, the smectic structure often occurs at the lower temperature. This is of course consistent with the greater degree of order within the smectic arrangement.

1.2.1. The Nematic Phase:

The nematic phase of calamitic liquid crystals is the simplest liquid crystal phase. In this phase, the molecules maintain a preferred orientational direction as they diffuse throughout the sample. The name "*nematic*" comes from the Greek word for thread, since in a polarizing microscope, there are often many dark lines visible in thick film samples. These lines are defects in the orientational order and are called disclinations. The preferred direction is undefined at these disclinations.

In the nematic phase, the long molecular axis tends to point along a preferred direction as the molecules undergo diffusion. This preferred direction is called the "*director*" and is denoted by the unit vector "n". Since consistence of alignment of molecules determines the degree of anisotropy, both "+n" and "-n" are equivalent. The molecules in this structure are associated in a head-to-tail fashion forming mobile threads that extend for several thousand-molecule lengths. A snapshot of elongated molecules in such a phase is shown in Figure 1.4.

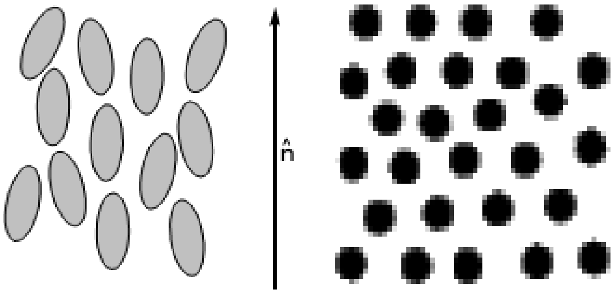

Figure 1.4. *Molecular order in nematic liquid crystals.*