SYNTHESIS AND STRUCTURE OF SUBSTITUTED PYRIDINE-BASED DERIVATIVES AND THEIR SUPRAMOLECULAR HYDROGEN – BONDED LIQUID CRYSTALS

Submitted for the

Partial Fulfillment of the requirements of M.Sc. degree in Organic Chemistry

By

Wedad Ali Almllal

B.Sc. in Chemistry

Department of Chemistry
Faculty of Science
Cairo University

2009

Approval sheet for submission

Title of the thesis

Synthesis and Structure of Substituted Pyridine-based Derivatives and their Supramolecular Hydrogen-bonded liquid crystals

Name of the candidate

Wedad Ali Almllal.

This Thesis has been approved for submission by the supervisors:

1- Prof. Dr. Abdelgawad Ali Fahmi.
Signature:

2- Prof. Dr. Magdi M. Naoum.
Signature:

Prof. Dr. Mohamed M. Shoukry.

Chairman, Department of Chemistry
Faculty of science – Cairo University

Cairo University
Faculty of Science

TO WHOM IT MAY CONCERN

This is to certify that Wedad Ali Almllal has attended and passed the following post graduate courses as a partial fulfillment of the requirements of the degree of master of science.

1- Quantum chemistry.
2- Molecular structure.
3- Advanced applied spectroscopy.
4- Physical organic chemistry.
5- Heterocyclic chemistry.
6- Photo chemistry.
7- Dyes.
8- Biochemistry.
9- Designing organic reactions.
10- Molecular orbital symmetry.
11- Carbohydrates.
12- Fluorine chemistry.
13- Polymer chemistry.
14- German language.

This certificate is issued at his own request.

Dedication

To

My lovely parents

For their role in my life, care, and love.

My sisters and brothers

For their overwhelming support and sympathy.

For all the things they've given me, I dedicate this thesis to them.

Acknowledgment

First, I thank our merciful **GOD** for his innumerable and diverse blessings and for helping me to accomplish this work.

I would like to express my deep gratitude to ***Prof.Dr. Abdelgawad Ali Fahmi***, Professor of Organic Chemistry, Department of Chemistry, Cairo University, for his valuable comment , encouragement, helpful notices and supervision.

I would like to express my sincere appreciation to ***Prof.Dr. Magdi M. Naoum***, Professor of Physical Chemistry, in the same Department, for his kindness, guidance, supervision and assistance throughout the various stages of the thesis.

My thanks is extend to ***Dr. Mohammed Alaasar*** for his help.

I wish to thank all friends in Libya and Egypt, especially, ***Rania Seoudi*** for her sincere advice.

At last, but not least at all. I offer my deepest thanks and recognition to ***my family*** for their patience, warm encouragements, and contineous support and love.

Wedad Ali Almllal.

Abstract

Name: Wedad Ali Almllal

Title of the thesis: Synthesis and Structure of Substituted Pyridine-based Derivatives and their Supramolecular Hydrogen-bonded liquid crystals

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

Six laterally methyl-substituted pyridine-based derivatives (**I**$_{a-f}$) of the type 4-(4'-pyridylazo-3-methylphenyl)-4''-substituted benzoates having the molecular formula 4-X-$C_6H_4COOC_6H_3$(3-CH_3)-N=N-C_5H_4N, were prepared and characterized. The substituent, X, varies between CH_3O, CH_3, H, Cl, Br, and CN. Two groups of the 1:1 complexes between the prepared derivatives (**I**$_{a-f}$) and 4-substituted benzoic acids (**II**) were prepared to investigate the effect of terminal substituents, either on the pyridine-based derivative or on the acid component, on the extent and stability of the supramolecular liquid crystal phases induced by intermolecular hydrogen bonding. In the first series of complexes (Group **A**), the non-mesomorphic pyridine-based derivative is complexed with the mesomorphic benzoic acid complement that carries an alkoxy group of varying chain length. Complexes of the other series (Group **B**) are composed of the same pyridine-based derivatives, but the benzoic acid complement carries small compact polar groups. In group **B** supramolecular complexes, neither of the pyridine-based derivative nor the acid complement is mesomorphic, but the hydrogen-bonded complexes are. The complexes prepared in both series were characterized for their mesophase behavior by differential scanning calorimetry, DSC, and polarized light microscopy, PLM. Five 4-alkoxybenzoic acids (4-$C_nH_{2n+1}O$-C_6H_4COOH, **II***8*-**II***16*) were used in group **A** complexes, while seven 4-substituted benzoic acids (Y-C_6H_4COOH, **II**$_{a-g}$) were used in group **B** complexes; the substituent Y varies between CH_3O, CH_3, H, Cl, Br, CN and NO_2. Smectic C mesophase of the acid is retained in group **A** complexes, while the nematic phase is induced in some of group **B** complexes.

Keywords: Supramolecular LCs, binary mixtures, 4-(4'-pyridylazo-3-methylphenyl)-4''-substituted benzoates, 4-substituted benzoic acids.

supervisors:

1- Prof. Dr. Abdelgawad Ali Fahmi.
Signature:
2- Prof. Dr. Magdi M. Naoum.
Signature:

Prof. Dr. Mohamed M. Shoukry.

Chairman, Department of Chemistry
Faculty of science – Cairo University

CONTENTS

LIST OF FIGURES

LIST OF TABLES

Chapter 1

INTRODUCTION TO LIQUID CRYSTALS

Liquid crystals [12] are intermediate states of matter, or mesophases, halfway between an isotropic liquid and a solid crystal. In nature, some substances, or even mixtures of substances, represent these mesomorphic states. This picture leads to the concept of ordering [13]. In a solid crystal, the basic units display translational long-range order, with the center of mass of atoms or molecules located on a crystal lattice; in some cases, the basic units also display orientational order. In an isotropic liquid, the basic units do not present either positional or orientational long- range order. From one ordering limit (solid crystal) to the other (isotropic liquid), there may exist many different situations. In plastic crystals, the basic units (e.g. globular molecules) are located on a lattice but without any orientational order. In liquid crystals (LC), the basic units display orientational order and even positional order along some directions. Liquid crystalline materials flow like an isotropic fluid and have characteristic optical properties of solid crystals. Such intermediate or mesophases are identified as being a true phase with definite transition temperatures and possesses considerable anisotropy that makes them distinct among ordinary liquids. This term *"Mesophase"* , and the associated terms *"Mesomorphs"* ,*"Mesomorphism"* , *"Mesomorphic"* ,and *"Mesoform"* are indeed widely used today, although references to liquid crystals are still frequently encountered in the literature.

The first observations of liquid crystalline or mesomorphic behavior were made toward the end of the 19 th century by Reinitzer [14] and Lehmann [15]. Since then, several thousands of organic compounds are known to form liquid crystals [16].

The amount of order in a liquid crystal is quite small relative to a crystal [17]. In a liquid crystal, there is only a slight tendency for the molecules to point more in one direction than others or to spend more time in various positions than others. 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 latent heat (values are around 250 J/g) which is very typical of a crystal to isotropic liquid transition. However, when a liquid crystal transforms to an isotropic liquid, the latent heat is much smaller, typically about 5 J/g.

1.1. Types of Liquid Crystals:

Liquid crystalline materials, in general, may have various types of molecular structures. What they all have in common is that they are anisotropic. That is, the shape is such that one molecular axis is very different from the other two. In such case, the interactions between these anisotropic molecules promote orientational and sometimes positional order in an otherwise fluid phase.

Liquid crystals are classified as "*Thermotropics*" and "*Lyotropics*", depending on the physico-chemical parameters responsible for the phase transitions. According to their mode of formation, "*Thermotropic Liquid Crystals*", are directly produced from solids by melting, or from the melt by cooling, while "*Lyotropic Liquid Crystals*", are those formed by mixing one or more components with a solvent.

1.1.1. Thermotropic Liquid Crystals:

In thermotropic liquid crystals the basic units are molecules, and the phase transitions depend on temperature and pressure. The mesomorphic and physical properties of thermotropic liquid material, 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.

A pronounced shape anisotropy is the main feature of the molecules which gives rise to a thermotropic mesophase. Beside pure substances, mixtures of molecules can also exhibit thermotropic mesomorphic properties. Thermotropic LCs are widely used in displays of low energy cost and in many sensor devices.

The thermotropic LCs could be further classified, according to the relative length of their molecular axes into calamitic (*rod-like*), discotic (*disc-like*), and banana shaped liquid crystals.