Republic of Iraq Ministry of Higher Education And Scientific Research Al-Nahrain University College of Science Department of Chemistry



# Synthesis and characterization of di- and tri- substituted benzamide derivatives as bis-swallow-tailed mesogens

A Thesis

Submitted to the College of Science Al-Nahrain University In partial fulfillment of the requirements for The Degree of Master of Science in Chemistry

# By

# **Donya Malek Hadi**

**B.Sc. 2014** 

Supervised By Assist. Prof. Dr. Nasreen R. Jber

Jan. 2017

Rabia-Althani 1438

# Supervisor certification

I certify that this thesis entitled "**Synthesis and characterization of diand tri- substituted benzamide derivatives as bis-swallow-tailed mesogens**" was prepared by "**Donya Malek Hadi**" under our Supervision at the of College of Science/ Al-Nahrain University as a partial requirements for the Degree of Master of Science in Chemistry.

Signature: Name: **Dr. Nasreen R. Jber** Scientific Degree: Assistance Professor Date: / / 2017

In view of the available recommendation, I forward this thesis for debate by the Examining Committee.

Signature: Name: **Dr. Emad Al-Sarraj** Scientific Degree: Professor Head of the Department of Chemistry College of Science Al-Nahrain University Date: / / 2017

# Examining Committee's Certification

We, the examining committee certify that we have read this thesis entitled "Synthesis and characterization of di- and tri- substituted benzamide derivatives as bis-swallow-tailed mesogens" and examined the student "Donya Malek Hadi" in its contents and that in our opinion, it is accepted for the degree of Master of Science in chemistry.

Signature: Name: **Dr. Mehdi S. Shihab** Scientific Degree: Professor Date: / /2017 (Chairman)

Signature: Name: **Dr. Ivan Hameed R. Tomi** Scientific Degree: Assistant Professor Date: / /2017 (Member) Signature: Name: **Dr. Sameaa J. khammas** Scientific Degree: Assistant Professor Date: / /2017 (Member)

Signature: Name: **Dr. Nasreen R. Jber** Scientific Degree: Assistant Professor Date: / /2017 (Member/Advisor)

I hereby certify upon the decision and the Examining Committee

Signature: Name: **Dr. Hadi M. A. Abood** Scientific Degree: Professor Title: Dean of the College of Science Date: / / 2017

التدارحم الرحم



صدق الله العلي العظيم سورة الفتح الآية 1 Dedicated ... To you

# Acknowledgement

My beloved family thank you for being a source of joy in my life... all my happiness comes from you. You have filled my life with color and meaning.
I would like to express the deepest appreciation to my supervisor Assist. Prof. Dr.
Nasreen R. Jber for help, guide and encouragement in every step of this work. Her guidance helped me in all the time of research and writing of this thesis.
My closest friends know who they are... thank you for being my best supporters and for all the fun we have had over the last years.
I am grateful for assistance given to me by the staff of Chemistry Department. Thank you all for just being here for me.

Donya

# **Contents**

	List of schemes	III
	List of tables	IV
	List of figures	V
	Summary	IX
	Chapter One: Introduction and Literature Review	
1.1	Liquid crystals	1
1.2	Characterization of Liquid Crystals	2
1.3	Structural Features of Liquid Crystals	2
1.4	History of Liquid Crystal Discovery	4
1.5	Classification of liquid crystal phases	6
1.6	Thermotropic liquid crystals	7
1.6.1	Liquid Crystals Phases	7
1.6.1.1	Nematic phase	7
1.6.1.2	Smectic Phase	8
1.6.1.3	Cholesteric phase	9
1.7	Lyotropic liquid crystals	10
1.8.1	Swallow-tailed mesogen	11
1.8.2	Bis-swallow-tailed mesogen	11
1.9	Applications of Liquid Crystals	12
1.10	Amides	13
1.11	Literature Survey	14
1.12	The aim of the work	16
Chapter Two: Experimental		
2.1	Chemicals	17

2.2	Techniques	17
2.3	Procedures of the step-wise synthesis	19
2.3.1	Preparation of n-alkylbromide (3)	19
2.3.2	Synthesis of 3,5-dialkyloxy and 3,4,5-trialkoxy benzoic acid (4,	19
	5)	
2.3.3	Preparation of 3,5-dialkoxy and 3,4,5-trialkoxybenzoyl chloride	20
	(6,7)	
2.3.4	Synthesis of compounds (10, 11, 12, 13)	20
2.3.5	Preparation of 4-alkyloxy benzoic acids (14)	21
2.3.6	Preparation of 4-alkyloxy benzoylchloride (15)	22
2.3.7	Synthesis of 3,5-di(4`-alkoxybenzoyl) benzoic acid (16)	22
2.3.8	Synthesis of 3,5-di(4`-alkoxybenzoyloxy) benzoylchloride (17)	23
2.3.9	Synthesis of compounds (18, 19)	23
2.3.10	Synthesis of N,N <sup>-4,4<sup>-</sup></sup> -biphenyl-bis[3 <sup>,4</sup> ,5 <sup>-</sup> -	24
	trihydroxybenzoic acid] and N,N'-1,4-phenyl-bis[3`,4`,5`-	
	trihydroxybenzoic acid] (20,21)	
2.3.11	Synthesis of N,N`-4,4`-biphenyl-bis[3``,4``,5``-tri(4```-	25
	alkoxybenzoyloxy)benzamide] and N,N'-1,4-phenyl-bis[3`,4`,5`-	
	tri(4``-alkoxybenzyloxy)benzamide](22,23)	
	Chapter three: Results and Discussion	
3.1	Synthesis of N,N <sup>-4,4<sup>-</sup></sup> -biphenyl-bis[3 <sup>,5</sup> ,5 <sup>-</sup>	27
	dipropoxybenzamide] (10), N,N <sup>-1</sup> ,4-phenyl-bis[3 <sup>,5</sup> -	
	dipropoxybenzamide] (11), N,N <sup>-4</sup> ,4 <sup>-biphenyl-bis[3<sup>,</sup>,4<sup>,</sup>,5<sup>,</sup>-</sup>	
	tripropoxybenzamide] (12) and N,N <sup>-1,4</sup> -phenyl-bis[3 <sup>,4</sup> ,5 <sup>-</sup>	
	tripropoxybenzamide] (13)	

3.2	Synthesis of N,N <sup>-4</sup> ,4 <sup>-biphenyl-bis[3<sup>-</sup>,5<sup>-</sup>di(4<sup>-</sup>)</sup>	38	
	alkyloxybenzoyloxy) benzamide] (18) and N,N <sup>-1,4</sup> -phenyl-		
	bis[3`,5`-di(4``-alkyloxybenzoyloxy) benzamide] (19)		
3.3	Synthesis of N,N <sup>-4</sup> ,4 <sup>-biphenyl-bis[3<sup>,4</sup>,4<sup>,5</sup>,5<sup>,+</sup>tri(4<sup>,1</sup>)</sup>	48	
	alkyloxybenzoyloxy) benzamide] (22) and N,N`-1,4-phenyl-		
	bis[3`,4`,5`-tri(4``-alkyloxybenzoyloxy) benzamide] (23)		
3.4	Thermotropic Liquid Crystalline Properties of synthesized	56	
	compounds		
3.4.1	Phase Transitions	56	
3.4.2	Phase structure	60	
3.5	Photoluminesce Spectra	62	
	References		
	References	65	

List of schemes		
3.1	Mechanism steps for preparation of 3,5-dipropoxy and 3,4,5-	27
	tripropoxybenzoic acid	
3.2	Mechanism steps for preparation of 3,5-dipropoxy and 3,4,5-	29
	tripropoxybenzoyl chloride (6) and (7)	
3.3	The synthetic pathway for compounds N,N`-1,4-phenyl-bis[3`,5-	31
	dipropoxybenzamide] (10).	
3.4	the synthetic pathway 3,5-di(4`-alkoxybenzoyloxy)benzoic acid	38
	(16)a-e	
3.5	the synthetic pathway N,N <sup>-4</sup> ,4 <sup>-</sup> -biphenyl-bis[3 <sup>,</sup> ,4 <sup>,</sup> ,5 <sup>,</sup> -	48
	tri(hydroxy)benzamide] (20) and N,N`-1,4-phenyl-bis[3`,4`,5`-	
	tri (hydroxy) benzamide] (21)	

	List of tables		
2.1	Physical properties of the compounds [4], [5]	20	
2.2	Physical properties of the compounds [10], [11], [12] & [13]	21	
2.3	Physical properties of the compounds [16a-e]	23	
2.4	Physical properties of the compounds [18a-e]	23	
2.5	Physical properties of the compounds [19a-e]	24	
2.6	Physical properties of the compounds [22a-e]	25	
2.7	Physical properties of the compounds [23a-e]	26	
3.1	Characteristic FT-IR absorption bands of synthesizes	40	
	compounds (16)a-e		
3.2	Characteristic FTIR absorption bands (cm <sup>-1</sup> ) of synthesized	44	
	compounds (18)a-e		
3.3	Elemental Analysis (CHN) for compounds (18)a,c,d	44	
3.4	Characteristic FTIR absorption bands (cm-1) of synthesized	45	
	compounds (19)a-e		
3.5	Elemental Analysis (CHN) for compounds (19)a, e	45	
3.6	The Elemental Analysis (CHN) for compounds 22a,b	52	
3.7	Characteristic FTIR absorption bands (cm-1) of synthesized	52	
	compounds (22)a-e		
3.8	The Elemental Analysis (CHN) for compounds [23] a,c	53	
3.9	Characteristic FTIR absorption bands (cm-1) of synthesized	53	
	compounds [23]a-e		
3.10	Melting points and type of transition for compounds (18)a-e	57	
3.11	Melting points and type of transition for compounds (19)a-e	58	
3.12	Melting points and type of transition for compounds (22)a-e	59	
3.13	Melting points and type of transition for compounds (23)a-e	59	

List of figures		
1.1	States of matter	1
1.2	Typical shape of a liquid crystal molecule	3
1.3	Alignment of the molecules for solid, liquid crystal and liquid	5
	phase	
1.4	Classification of liquid crystals	6
1.5	Molecular arrangement of nematic phase	8
1.6	The smectic A phase (left) has molecules arranged into layers. In	9
	the smectic C phase (right), the molecules are leaned inside the	
	layers.	
1.7	Molecular arrangement of Cholesteric phase	10
1.8	Amide preparation	13
1.9	a new homologous series of Schiff base esters comprising a	14
	terminal alkoxy substituent.	
1.10	3-alkoxy-2-(alkoxymethyl)-1-propyl 4-(4'alkoxybiphenyl-4-	15
	carbonyloxy)benzoates	
1.11	4,4`-(dihexyloxybenzoate)-diphenylether.	15
1.12	series of six-ring double-swallow-tailed mesogens	16
3.1	FT-IR spectrum of 3,5-dipropoxybenzoic acid (4)	28
3.2	FT-IR spectrum of 3,4,5-tripropoxybenzoic acid (5)	29
3.3	FT-IR spectrum of 3,5-dipropoxybenzoyl chloride (6)	30
3.4	FT-IR spectrum of N,N <sup>-4</sup> ,4 <sup>-</sup> -biphenyl-bis[3 <sup>-</sup> ,5 <sup>-</sup> -	32
	dipropoxybenzamide] (10)	
3.5	FT-IR spectrum of N,N <sup>-1</sup> ,4-phenyl-bis[3 <sup>,5</sup> -	32
	dipropoxybenzamide] (11)	

3.6	<sup>1</sup> H-NMR spectrum of N,N`-4,4`-biphenyl-bis[3``,5``-	34
	dipropoxybenzamide] (10)	
3.7	FT-IR spectrum of N,N`-4,4`-biphenyl-bis[3``,4``,5``-	35
	tripropoxybenzamide] (12)	
3.8	FT-IR spectrum of N,N`-1,4-phenyl-bis[3`,4`,5`-	36
	tripropoxybenzamide] (13)	
3.9	<sup>1</sup> H-NMR spectrum of N,N`-4,4`-biphenyl-bis[3``,4``,5``-	37
	tripropoxybenzamide] (12)	
3.10	FT-IR spectrum of 3,5-di-(4`-pentoxybenzoyloxy)benzoic acid	39
	(16)c	
3.11	FT-IR spectrum of 3,5-di-(4`-propoxybenzoyloxy)benzoic acid	38
	(16)a	
3.12	FT-IR spectrum of 3,5-di-(4`-octyloxybenzoyloxy)benzoic acid	40
	(16)e	
3.13	FT-IR spectrum of N,N`-4,4`-biphenyl-bis[3``,5``-di(4```-	41
	pentoxybenzoyloxy) benzamide] (18)c	
3.14	FT-IR spectrum of N,N <sup>-4</sup> ,4 <sup>-</sup> -biphenyl-bis[3 <sup>,5</sup> ,5 <sup>,-</sup> di(4 <sup>,</sup> )	42
	heptoxybenzoyloxy)benzamide] (18)d	
3.15	<sup>1</sup> H-NMR spectrum of N,N`-4,4`-biphenyl-bis[3``,5``-di(4```-	43
	propoxybenzoyloxy) benzamide] (18)a	
3.16	FT-IR spectrum of N,N`-1,4-phenyl-bis[3`,5`-di(4``-	46
	propoybenzoyloxy)benzamide] (19)a	
3.17	FT-IR spectrum of N,N <sup>-1</sup> ,4-phenyl-bis[3 <sup>,5</sup> -di(4 <sup>,</sup> -	46
	propoybenzoyloxy)benzamide] (19)c	
3.18	<sup>1</sup> H-NMR spectrum of N,N`-1,4-phenyl-bis[3`,5`-di(4``-	47
	butoxybenzoyloxy) benzamide](19)b	
		1

3.19	FT-IR spectrum of N,N <sup>-4</sup> ,4 <sup>-</sup> -biphenyl-bis[3 <sup>-</sup> ,4 <sup>-</sup> ,5 <sup>-</sup> -tri(4 <sup>-</sup> )	49
	octyloxybenzoyloxy)benzamide] (22)e	
3.20	FT-IR spectrum of N,N`-4,4`-biphenyl-bis[3``,4``,5``-tri(4```-	49
	heptoybenzoyloxy) benzamide] (22)d	
3.21	<sup>1</sup> H-NMR spectrum of N,N`-4,4`-biphenyl-bis[3``,4``,5``-tri(4```-	51
	propoxybenzoyloxy)benzamide] (22)a	
3.22	FT-IR spectrum of N,N`-1,4-phenyl-bis[3`,4`,5`-tri(4``-	54
	octyloxybenzoyloxy) benzamide](23)d	
3.23	FT-IR spectrum of N,N`-1,4-phenylbis[3`,4`,5`-tri(4``-	54
	octylbenzoyloxy)benzamide](23)e	
3.24	<sup>1</sup> H-NMR spectrum of N,N'-1,4-phenyl-bis[3`,4`,5`-tri(4``-	55
	butyloxybenzoyloxy) benzamide](23)b	
3.25	Differential scanning thermogram of compounds 10, 11, 12 and	56
	13 as a function of temperature for the second heating and	
	cooling cycles (at scan rate 10 °C min <sup>-</sup> 1)	
3.26	Differential scanning thermogram of compound 18a and 18d as a	56
	function of temperature for the second heating and cooling	
	cycles (at scan rate 10 °C min <sup>-</sup> 1)	
3.27	Differential scanning thermogram of compound 19a and 19c as a	58
	function of temperature for the second heating and cooling	
	cycles (at scan rate 10 °C min <sup>-</sup> 1	
3.28	Differential scanning thermogram of compound 22d as a	59
	function of temperature for the second heating and cooling	
	cycles (at scan rate 10 °C min <sup>-</sup> 1)	
3.29	Differential scanning thermogram of compound 23e as a	60
	function of temperature for the second heating and cooling	
	cycles (at scan rate 10 °C min <sup>-</sup> 1)	

3.30	Spherical droplets nematic phase of compound 19c at 174 °C	61
	(magnification 10 x 10)	
3.31	Schlieren texture of the nematic phase of compound 22d at	61
	206°C (magnification 10 ×10)	
3.32	Schlieren texture of the nematic phase of compound 23c at	61
	206°C (magnification 10 ×10)	
3.33	The emission spectrum for the Xe lamp used to excite the	62
	studied samples	
3.34	The PL spectrum for compound (18)a	63
3.35	The PL spectrum for compound (19)c	63
3.36	The PL spectrum for compound (22)d	64
3.37	The PL spectrum for compound (23)c	64

## Summary

This study is concerned with the synthesis and characterization of some new liquid crystalline compounds derived from di- and tri-hydroxy benzoic acids with bis-swallow tailed which called  $N,N^-1,4$ -phenyl-bis[3`,5`-disubstituted benzamide],  $N,N^-4,4$ `-biphenyl-bis[3``,5``-disubstitutedbenzamide],  $N,N^-1,4$ -phenyl-bis[3`,4`,5`-trisubstitutedbenzamide] and  $N,N^-4,4$ `-biphenyl-bis[3``,4``,5``-tri substituted benzamide] which were synthesized according to the following schemes(1, 2, 3, 4):



Schem: 1



Schem: 2





The synthesized compounds were characterized using FT-IR, CHNS analysis and <sup>1</sup>H-NMR for some of them.The liquid crystalline properties of the prepared compounds, the effect of these ends on the mesogenic properties and their transitional stability were verified using hot-stage polarizing optical microscope (POM) and differential scanning calorimeter (DSC). The compounds show

photoluminescence properties in the organic solution at room temperature, with the fluorescence band centered around 400 nm.



# CHAPTER ONE

# Introduction



# **INTRODUCTION**

## **1.1 Liquid crystals**

What are liquid crystals? Liquid crystals are mesophases between crystalline solids and isotropic liquid<sup>(1)</sup>.



Figure 1.1 states of matter.

The distinguishing characteristic of the liquid crystalline state is the tendency of the molecules (mesogens) to point along a common axis, called the director. This is in contrast to molecules in the liquid phase, which have no intrinsic order. In the solid state, molecules are highly ordered and have little translational freedom. The characteristic orientational order of the liquid crystal state is between the traditional solid and liquid phases and this is the origin of the term "mesogenic state" used synonymously with liquid crystal state. Polymorphism arises between the transformation of crystal to isotropic fluid due to weak intermolecular forces that imparts the equilibrium, results in well-defined phase changes. This was known as mesomorphism and the phases known as 'mesophases'<sup>(2)</sup>. Liquid crystals are anisotropic materials whose flow properties strongly depend on their structures and molecular orientation<sup>(3)</sup>.

# **1.2 Characterization of Liquid Crystals**

The following parameters describe the liquid crystalline structure:

 $\cdot$  **Orientational order:** Measure of the tendency of the molecules to align along the director on a long-range basis.

• **Positional order:** The extent to which the position of an average molecule or group of molecules shows translational symmetry.

• **Bond orientational order:** Describes a line joining the centers of nearestneighbor molecules without requiring a regular spacing along that line. Thus, a relatively long range order with respect to the line of centers but only short range positional order along that line<sup>(4)</sup>.

Each of these parameters describes the extent to which the liquid crystal sample is ordered. Most liquid crystal compounds exhibit polymorphism, or a condition where more than one phase is observed in the liquid crystalline state. The term mesophase is used to describe the "subphases" of liquid crystal materials. Mesophases are formed by changing the amount of order in the sample, either by imposing order in only one or two dimensions, or by allowing the molecules to have a degree of translational motion<sup>(5)</sup>.

## **1.3 Structural Features of Liquid Crystals**

Certain structural features are often found in molecules forming liquid crystal phases, and they may be summarized as follows:

1. The molecules have anisotropic shape (e. g. are elongated). Liquid crystallinity is more likely to occur if the molecules have flat segments, e. g. benzene rings.

2. A fairly good rigid backbone containing double bonds.

3. The existence of strong dipoles and easily polarizable groups in the molecule seems important<sup>(6)</sup>.



Figure 1.2 Typical shape of a liquid crystal molecule.

Figure 1.2 shows the basic structures of the most commonly occurring liquid crystal molecules. They are aromatic and, if they contain benzene rings, they are often referred to as benzene derivatives. In general, aromatic liquid crystal molecules such as those shown in Figure 1.2 comprise a side chain R, two or more aromatic rings A and A', connected by linkage group X, and at the other end connected to a terminal group R'. Examples of side-chain and terminal groups are alkyl (CnH<sub>2n+1</sub>), alkoxy (CnH<sub>2n+1</sub>O), and others such as acyloxyl, alkylcarbonate, alkoxycarbonyl, and the nitro and cyano groups. The Xs of the linkage groups are simple bonds or groups such as stilbene (-CH=CH-), ester (RCO<sub>2</sub>R'), azoxy (-N=N-O-), Schiff base (-CH=N-), acetylene (-C $\equiv$ C-), and diacetylene (-C $\equiv$ C-C $\equiv$ C-). The names of liquid crystals are often fashioned after the linkage group (e.g., Schiff-base liquid crystal)<sup>(7)</sup>. Lateral substituents are often used to modify the mesophase morphology and the physical properties of liquid crystals to generate enhanced properties for applications. The units that are used in this general structure and their combinations determine the type of liquid crystal phase and the physical properties exhibited by a compound. A certain rigidity is required to provide the anisotropic molecular structure<sup>(8)</sup>.

# 1.4 History of Liquid Crystal Discovery

At the end of the 19th century Austrian scientist Fridrich Reinitzer<sup>(9)</sup> studied two substances extracted from carrot, namely light-colored hydrocarotin and dark-red carotin, he synthesized and studied nitrocholesterol and cholesterol benzoate. Two esters, namely cholesterol acetate and cholesterol benzoate, were of special interest. Both substances in the solid phase are white fine-crystalline powders. When Reinitzer determined the melting temperature he saw that they became colored. At that time nobody understood that strange fact of coloring of colorless compounds in melting. Reinitzer found two melting points of cholesterol benzoate. He managed to find that at a temperature of 145.5 °C the white fine cholesterol benzoate powder transformed into a turbid, hardly transparent liquid. As cholesterol benzoate was heated further, the turbidity disappeared suddenly. This occurred at 178.5 °C <sup>(10)</sup>. Reinitzer turned for help to the German physicist Otto Lehmann, who was an expert in crystal optics. Lehmann became convinced that the cloudy liquid had a unique kind of order. In contrast, the transparent liquid at higher temperature had the characteristic disordered state of all common liquids. Eventually he realized that the cloudy liquid was a new state of matter and coined the name "liquid crystal". Illustrating that it was something between a liquid and a solid, sharing important properties of both. In a normal liquid the properties are isotropic, i.e. the same in all directions. In a liquid crystal they are not; they strongly depend on direction even if the substance itself is fluid<sup>(11)</sup>. The alignment of the molecules for each phase showed in the figure 1.3.



#### •

#### Figure 1.3 Alignment of the molecules for solid, liquid crystal and liquid phase.

In 1922 the French scientist Friedel produced the first classification scheme of liquid crystals<sup>(12)</sup>, dividing them into three different types of mesogens (materials able to sustain mesophases), based upon the level of order the molecules possessed in the bulk material:

- 1. Nematic (from the Greek word nematos meaning "thread"),
- 2. Smectic (from the Greek word smectos meaning "soap"), and
- 3. Cholesteric (better defined as chiral nematic) $^{(13)}$ .

# **1.5 Classification of liquid crystal phases**

Liquid crystals can be first organized into Thermotropic (temperature dependent) and Lyotropic (concentration dependent). The classification of liquid crystals is shown in Figure 1.4.



Figure 1.4 Classification of liquid crystals.

# **1.6 Thermotropic liquid crystals**

As the name suggests, thermotropic liquid crystals are formed due to the effect of heat<sup>(10)</sup>. Thermotropic liquid crystalline phases are exhibited by large number of organic compounds whose molecule has anisotropy of shape. This state can be obtained by raising temperature of solids and/lowering temperature of liquid. If temperature increase is too high, thermal motion will destroy ordering of liquid crystal phase, pushing material into isotropic liquid phase. If temperature is too low, most liquid crystal materials will form conventional crystals<sup>(14)</sup>.

# **1.6.1 Liquid Crystals Phases**

### 1.6.1.1 Nematic phase

These are the simplest type of liquid crystalline materials<sup>(15)</sup>. The word nematic is derived from the Greek word "Nema" meaning thread like. Under the polarsing microscope, the nematic phase is seen as thread schlieren texture<sup>(16)</sup>. This is the most liquid like structure in which, contrary to isotropic liquids, one or two molecular axes are oriented parallel to one another resulting in an orientational longrange order and short positional order. Molecules can rotate by both the axes, the molecules have several possibility of intermolecular mobility. Because of the high mobility, the nematic phases have low viscosities. They are anisotropic with respect to optical properties, viscosity, electrical and magnetic susceptibility, electrical and thermal conductivity.



Figure 1.5 Molecular arrangement of nematic phase.

#### **1.6.1.2 Smectic Phase**

The smectic phases, which are found at lower temperatures than the nematic, form well-defined layers that can slide over one another in a manner similar to that of soap. The word "smectic" originates from the Latin word "smecticus", meaning cleaning, or having soap-like property <sup>(17)</sup>. The important feature of the smectic phase, which distinguishes it from the nematic, is it's stratification. The molecules are arranged in layers and exhibit some correlations in their positions in addition to the orientational ordering<sup>(6)</sup>. The smectics are thus positionally ordered along one direction. In the Smectic C phase, the molecules are oriented along the layer normal, while in the Smectic C phase they are tilted away from the layer normal. These phases are liquid-like within the layers. There are many different smectic phases, all characterized by different types and degrees of positional and orientational order<sup>(18)</sup>.



Figure 1.6 The smectic A phase (left) has molecules organized into layers. In the smectic C phase (right), the molecules are tilted inside the layers.

## 1.6.1.3 Cholesteric phase

The name is based on the fact that derivatives of the infamous cholesterol were initially found to exhibit this phase<sup>(18)</sup>. Cholestic (or chiral nematic) liquid crystal, resembles nematic liquid crystal in all physical properties except that the molecules tend to align themselves into a helical structure with the helical axis perpendicular to the director, as depicted in fig 1.7. The helical structure leads to a selective reflection in wavelength and circular polarization<sup>(19)</sup>. Nematic phases can be converted into chiral nematic phases by addition of a small amount of chiral (optically active) dopant. These mesophases are birefringent on account of the existent chirality<sup>(20)</sup>.



Figure 1.7 Molecular arrangement of Cholesteric phase.

## **1.7 Lyotropic liquid crystals**

Lyotropic liquid crystals result from the action of a solvent. When certain compounds are treated with a solvent. A true solution is not obtained and the resulting state possesses characteristics of the liquid crystalline phase. Lyotropic mesophases can be destroyed or converted into isotropic liquids by an excess of solvent or by heating to sufficiently high temperatures<sup>(21)</sup>. Lyotropic liquid crystals have several fundamental characteristics that make them dramatically different than thermotropic liquid crystals. First, these types of liquid crystals form in solution rather than in pure substances. Secondly, individual molecules do not align by themselves to create anisotropy instead, the molecules come together to form anisotropic aggregates which themselves align along director. For these reasons, additional conditions besides temperature determine whether the liquid crystals phase forms. Temperature still effects phase in the same way as thermotropic liquid crystals but concentration of substance also has strong effect on liquid crystalline behavior. Lyotropic crystals are formed by the amphiphilic molecules, often known as surfactants. These two types of liquid crystals are distinguished by mechanisms that drive self-organization, but they are also similar in many ways. Thermotropic phases are initiated by changes in temperature, while lyotropic phases can also be initiated by changes in concentration<sup>(14)</sup>.

#### **1.8.1 Swallow-tailed mesogen**

Mesogen composed of molecules each with an elongated rigid core, with branches of about the same length, attached at each end.

A sketch of the structure of a swallow-tailled mesogen is<sup>(22)</sup>:



#### **1.8.2 Bis-swallow-tailed mesogen**

Double swallow-tailed compounds are special cases of tetracatenar mesogens (mesogens consisting of a rod-like core and two half-disc shaped moieties), where the branches are not attached directly to the terminal rings. Experiments are reported in which the middle part of the core and the length of the terminal chains were varied. The resulting effects on the transition temperatures and phase behavior are described and trends pointed out<sup>(22)</sup>.



# **1.9** Applications of Liquid Crystals

Liquid crystals have attracted a lot of attention due to the unique electrooptical and thermo-optical properties and have been used in numerous applications<sup>(23)</sup>. Research on optical & electrical properties of these unique compounds attracted very much by scientific and industrial community. Later, research at a number of industries, universities and government laboratories began to focus on their applications, which exploited the electro-magneto-optic characteristics and photoelectric properties of nematic and cholesteric type liquid crystals. Now a days liquid crystals are widely used in cosmetic industry in manufacturing of liquid crystal makeup removers, lipsticks and lip glasses containing cholesteric liquid crystals. Liquid crystals are using extensively in pharmaceutical industries. Liquid crystal displays are common in calculators, digital watches, oscillaographic systems, television displays using L.C. screens has also been developed. Cholesteric liquid crystals have also been used for novelty items such as toys and decorative materials<sup>(24)</sup>. The temperaturedependent variation in the color of cholesteric liquid crystals has led to the use of these substances in the measurement of temperature gradients. Cholesteric liquid crystal substances, when applied to the surface of the skin, have been used to locate veins, arteries, infections, tumors and the fetal placenta which are warmer than the surrounding tissues. Nematic liquid crystal are useful research tools in the application of magnetic resonance. Molecules that are dissolved in nematic liquid crystal solvents give a very highly resolved NMR spectrum exhibiting intermolecular dipole-dipole fine structures. Analysis of the spectra of molecules in liquid crystal solvents yield information regarding the anisotropy of chemical shifts, direct magnetic dipole-dipole interaction, indirect spin-spin couplings, bond angles, bond lengths, molecular order and relaxation process. Liquid crystals have been used in chromatographic separations as solvents to direct the course of chemical reactions and to study molecular arrangements and kinetics and as anisotropic host fluid for visible, UV and IR spectroscopy of organic molecules<sup>(25)</sup>.

#### 1.10 Amides

Most common of organic amides are carboxamides, as well as, phosphoramides and sulfonamides are known important amide sorts. Amides are pervasive in nature and technology as structural materials. Many methods exist in amide synthesis. The simplest method for making amides is by coupling a carboxylic acid with an amine. Coupling reactions with acyl chlorides could be formed amide bond by reacting the acyl chloride with the desired amine (Aminolysis) as shown in figure 1.8. An additional base is usually required to trap the formed HCl and to avoid the conversion of the amine into its unreactive HCl salt. Couplings are usually performed in inert dry solvents, in the presence of a non-nucleophilic tertiary amine (NEt3, iPr2NEt (also called Hunig's base), or N-methylmorpholine). However, acyl chlorides are often robust enough to be coupled to amines under aqueous conditions, for example, in the presence of NaOH (Schotten–Baumann conditions)<sup>(26)</sup>.



Figure 1.8 amide preparation.

# **1.11 Literature Survey**

In 2014, Nasreen R. et. Synthesized a new homologous series of Schiff base esters comprising a terminal alkoxy substituent N-{(n-alkoxy-4``-bezoyloxy)-4`-benzylidene}-4-butyl aniline. The alkyloxy substituent contributes to the molecular polarizability, thus, affecting intermolecular interactions, hence, resulting in nematic polymorphism. The mesomorphic properties were studied using polarizing optical microscope (POM)<sup>(27)</sup>.



Figure 1.9 a new homologous series of Schiff base esters comprising a terminal alkoxy substituent.

In 2007, kyung-Tae Kang et. Synthesis New liquid crystalline (biphenylcarbonyloxy)benzoates with an achiral swallow-tail derived from 3-alkoxy-2(alkoxymethyl)-1-propanol [(ROCH 2 ) 2 CHCH 2 OH, R = Me, Et, Pr, Bu]. These liquid crystals exhibited the phase sequence (I-SmA-SmCalt-(SmCX)-Cr) and showed antiferroelectric-like Smectic C phase (SmCalt) at temperature lower, and temperature range broader than do the compounds containing a

branched alkyl group as a swallow-tail. The temperature ranges of antiferroelectric phase were found to be 30-90 °C and crystallization temperatures were 4-60 °C. The binary mixture of an achiral swallow-tailed liquid crystal and a chiral antiferroelectric liquid crystal, (S)-MHPOBC showed antiferroelectric smectic C phase at temperature much lower than the single chiral antiferroelectric liquid crystal does<sup>(28)</sup>.



Figure 1.10 3-alkoxy-2-(alkoxymethyl)-1-propyl 4-(4'alkoxybiphenyl-4carbonyloxy)benzoates.

In 2013 Liquid crystal with bent core-tail substitution geometry synthesize through esterification of 4,4'-dihydroxydiphenyl ether and 4-hexyloxybenzoic acid, using a standard DCC/DMAP procedure <sup>(29)</sup>.



Figure 1.11 4,4'-(dihexyloxybenzoate)-diphenylether.

In 1995 W. Weissflog and coworkers synthesized a new homologous series of six-ring double-swallow-tailed mesogens. Liquid-crystalline properties strongly depend on the length of the terminal alkyl chains<sup>(30)</sup>.



Figure 1.12 series of six-ring double-swallow-tailed mesogens.

#### **1.12** The aim of the work

The purposes of this study are:

- Synthesis some new type of compounds having mesogenic properties derived from Gallic and 3, 5-dihydroxy benzoic acid which called bis-swallow-tail mesogen.
- Characterization of the synthesized compounds using FT-IR and <sup>1</sup>H-NMR spectroscopy.
- Elucidate the liquid crystalline properties of the synthesized compounds using POM (polarizing optical microscope) and DSC (differential scanning calorimetry).
- Study the Luminescence effect of the highly conjugated synthesized compounds.



# CHAPTER TWO

**Experimental Part** 


#### EXPERIMENTAL

## **2.1 Chemicals**

The chemicals used were supplied from BDH, Fluka and Merck supplier companies.

# 2.2 Techniques

## 2.2.1 Fourier Transform Infrared Spectrophotometer (FT-IR)

FT-IR spectra in the range (4000-400) cm<sup>-1</sup> were recorded using potassium bromide disc on FT-IR instrument Model 8300 Shimadzu Spectrophotometer, Japan. The analysis were carried out in Al-Nahrain University.

# 2.2.2 Proton Nuclear magnetic resonance spectrometer (<sup>1</sup>H -NMR)

Proton Nuclear Magnetic Resonance (<sup>1</sup>H-NMR) spectra were recorded on Brüker ACF 300 spectrometer at 300 MHz, using deuterated chloroform (CDCl<sub>3</sub>), (d<sub>6</sub>-acetone) or (d<sub>6</sub>-DMSO) as solvent with TMS as an internal standard, in the University of Exeter, England.

# 2.2.3 Melting point

Uncorrected melting points were recorded on hot stage Gallen kamp melting point apparatus (U.K.).

# 2.2.4 Differential scanning calorimeter (DSC)

Transition temperatures and enthalpies were scanned by LINSEIS DSC PT-1000 differential scanning calorimeter with a heating rate of 10.0°C/min in air and it was calibrated with indium (156.6°C, 28.45 J/g) at Al Nahrain University and University of Exeter, England.

#### 2.2.5 Hot stage Polarizing Microscope

Liquid crystalline properties were investigated by using a (Meiji MT9000) Polarizing Optical Microscope attached to an INSTEC Hot stage. The texture of the compounds were observed using polarized light with crossed polarizers, the sample being prepared as a thin film sandwiched between a glass slide and a cover. A camera (Lumenera) was installed on the polarizing microscope. The analysis were carried out at Al-Nahrain University.

# 2.2.6 Elemental analysis (CHNS-O)

Elemental analysis (CHNS-O) was carried out using EURO EA elemental analyzer instrument. The analysis were carried out in Al-Nahrain University.

# 2.2.7 Spectrofluorometer

Fluorescence spectra were recorded by using excitation wavelengths corresponding to the peaks of their absorption diagrams by using (F96-pro). The analysis were carried out Laser engineering department at Al-Nahrain University.

## 2.3 Procedures of the step-wise synthesis

## 2.3.1 Preparation of n-alkylbromide (3):

The titled compounds were synthesized according to the literature A. Vocal<sup>(31)</sup>.

# 2.3.2 Synthesis of 3,5-dialkyloxy and 3,4,5-trialkoxy benzoic acid (4, 5):



Dissolving (0.01 mol) of 3,5-Dihydroxy benzoic acid in (20 mL) ethanol. (2.76 g, 0.03 mol)  $K_2CO_3$  was added with stirring, the mixture was placed in (100 mL) round bottom flask and cooled to room temperature, then (0.02 mol) of appropriate alkyl bromide was added drop wise. The solution was refluxed overnight. (2.78 g, 0.02 mol)  $K_2CO_3$  dissolved in a little amount of water (~ 5mL) was added to the reaction mixture and heated for (1-3) hours. The solvent was evaporated and equal volume of water was added. The solution was heated till became clear. Acidification with conc. HCl yielded precipitate. Recrystallization from ethanol gave the desired product<sup>(32)</sup>. 3,4,5-Trialkoxy benzoic acid was prepared in the same procedure using three moles of appropriate alkyl bromide instead of two moles.

No.	Name of compound	Chemical Formula	M.W. (g\mol)	Yield %	m.p °C	color
5	3,4,5-Tripropoxybenzoic acid	C <sub>16</sub> H <sub>24</sub> O <sub>5</sub>	296.39	94	171-173	Bright brown
4	3,5-Dipropoxybenzoicacid	$C_{13}H_{18}O_4$	238.28	92	165-168	Pale yellow

Table (2.1) Physical properties of the compounds [4], [5].

# 2.3. 3 Preparation of 3,5-dialkoxy and 3,4,5-trialkoxybenzoylchloride

# (6, 7):



The corresponding 3,5-Dialkoxy and 3,4,5-Trialkoxy benzoic acid (0.01 mol) were refluxed with thionyl chloride (5mL) and 2 drops of DMF for (3-4) hours. Excess of thionyl chloride was distilled off <sup>(33)</sup>.

# 2.3.4 Synthesis of compounds (10, 11, 12, 13):



A mixture of benzidine or *p*-phenylenediamine (0.01mol) and 3,5dialkoxybenzoylchloride (or 3,4,5- trialkoxybenzoylchloride) (0.02 mol) with (10 mL) pyridine were stirred for 24 hour in an ice bath. The mixture was poured onto cold water, acidification with HCl and filtered<sup>(34)</sup>.

No.	Name of compound	Chemical	M.W.	Yield	m.p	color
		Formula	(g\mol)	%	°C	
10	N,N`-4,4`-biphenyl-bis[3``,5``-	$C_{38}H_{44}N_2O_6$	624.76	80	188-190	brown
	dipropoxybenzamide]					
11	N,N`-1,4-phenyl-bis[3`,5`-	$C_{32}H_{40}N_2O_6$	548.66	80	164-168	Dark
	dipropoxybenzamide]					brown
12	N,N`-4,4`-biphenyl-bis[3``,4``,	$C_{44}H_{56}N_2O_8$	740.92	92	202-204	Dark
	5``-tripropoxybenzamide]					brown
13	N,N`-1,4-phenyl-bis[3`,4`,5`-	$C_{38}H_{52}N_2O_8$	664.82	70	192-195	Dark
	tripropoxybenzamide]					brown

Table (2.2) Physical properties of the compounds [10], [11], [12] and [13].

#### 2.3.5 Preparation of 4-alkyloxy benzoic acids (14):



4-Hydroxy benzoic acid (1.38 g, 0.1 mol) corresponding alkyl halides (0.12 mol) and KOH (0.25 mol) were dissolved in (10 mL) methanol and reaction mixture was refluxed for 3 to 4 hr. 10% aqueous KOH solution (20 mL) was added and refluxing continued for further two hours to hydrolysis any ester formed. The solution

was cooled and acidified with HCl to precipitate. The corresponding alkyloxy acids of the higher members the total refluxing period was extended to (7-8) hour<sup>(35)</sup>.

# 2.3.6 Preparation of 4-alkyloxy benzoylchloride (15):



The same procedure used as in 2.3.1.3 using 4-alkyloxy benzoic acids (0.1 mol) instead of 3,4,5-Trialkoxy benzoic acid (0.01mol)<sup>(33)</sup>.

# 2.3.7 Synthesis of 3,5-di(4`-alkoxybenzoyloxy) benzoic acid (16):



A mixture of 4-alkoxy benzoylchloride (0.02mol) and 3,5-dihydroxybenzoic acid (0.01mol) with (10 mL) pyridine were stirred for 24 hour in an ice bath. The mixture were poured in cold water and acidified with HCl and filtered <sup>(34)</sup>.

No.	Name of compound	Chemical	M.W.	Yield	m.p	color
		Formula	(g\mol)	%	°C	
16a	3,5-di[4`-propoxy benzoyloxy]benzoic acid	C <sub>27</sub> H <sub>26</sub> O <sub>8</sub>	478.49	74	254-272	brown
16b	3,5-di[4`-butoxy benzoyloxy]benzoic acid	$C_{29}H_{30}O_8$	506.54	68	263-281	brown
16c	3,5-di[4`-pentoxy benzoyloxy]benzoic acid	C <sub>31</sub> H <sub>34</sub> O <sub>8</sub>	534.59	77	203-218	brown
16d	3,5-di[4`-heptoxy benzoyloxy]benzoic acid	C35H42O8	590.70	70	189-205	brown
16e	3,5-di[4`-octoxy benzoyloxy]benzoic acid	C37H46O8	618.76	84	176-184	brown

Table (2.3) Physical properties of the compounds [16a-e].

# 2.3.8 Synthesis of 3,5-di(4`-alkoxybenzoyloxy) benzoylchloride (17):

The titled compounds synthesis as the same procedure used in  $2.3.1.3^{(33)}$ .

# 2.3.9 Synthesis of compounds (18, 19):

The same procedure used as in 2.3.1.4 using benzidine or *p*-phenyldiamine (0.005 mol) and 3,5-di(4<sup>-</sup>alkoxybenzoyloxy) benzoylchloride  $(0.01 \text{ mol})^{(34)}$ .

No.	Name of compound	Chemical	M.W.	Yield	m.p	color
		Formula	(g\mol)	%	°C	
18a	N,N`-4,4`-biphenyl-bis[3``,5``-di(4```-	$C_{66}H_{60}N_2O_{14}$	1105.2	64	261-	Dark
	propoxy benzoyloxy)benzamide]				279	brown
18b	N,N <sup>-4</sup> ,4 <sup>-biphenyl-bis[3<sup>-</sup>,5<sup>-</sup>di(4<sup>-</sup>)</sup>	$C_{70}H_{68}N_2O_{14}$	1161.2	70	243-	Dark
	butoxy benzoyloxy)benzamide]				257	brown

Table (2.4) Physical properties of the compounds [18a-e].

18c	N,N`-4,4`-biphenyl-bis[3``,5``-di(4```-	$C_{74}H_{76}N_2O_{14}$	1217.4	77	212-	Dark
	pentoxy benzoyloxy)benzamide]				229	brown
18d	N,N <sup>-4</sup> ,4 <sup>-biphenyl-bis[3<sup>,5</sup>,5<sup>,-</sup>di(4<sup>,1</sup>)</sup>	$C_{82}H_{92}N_2O_{14}$	1329.6	72	208-	Dark
	heptoxy benzoyloxy)benzamide]				218	brown
18e	N,N`-4,4`-biphenyl-bis[3``,5``-di(4```-	$C_{86}H_{100}N_2O_1$	1385.7	69	196-	Dark
	octyloxy benzoyloxy)benzamide]	4			206	brown

Table (2.5) Physical properties of the compounds [19a-e].

No.	Name of compound	Chemical	M.W.	Yield	m.p	color
		formula	(g\mol)	%	°C	
19a	N,N`-1,4-phenyl-bis[3`,5`-di(4``-	$C_{60}H_{56}N_2O_{14}$	1029.1	76	216-221	Dark
	propoxybenzoyloxy) benzamide]					brown
19b	N,N`-1,4-phenyl-bis[3`,5`-di(4``-	$C_{64}H_{64}N_2O_{14}$	1082.2	58	206-211	Dark
	butoxybenzoyloxy) benzamide]					brown
19c	N,N`-1,4-phenyl-bis[3`,5`-di(4``-	$C_{68}H_{72}N_2O_{14}$	1141.3	66	201-210	Dark
	pentoxybenzoyloxy) benzamide]					brown
19d	N,N`-1,4-phenyl-bis[3`,5`-di(4``-	$C_{76}H_{88}N_2O_{14}$	1253.5	83	194-198	Dark
	heptyloxybenzoyloxy) benzamide]					brown
19e	N,N`-1,4-phenyl-bis[3`,5`-di(4``-	C <sub>80</sub> H <sub>96</sub> N <sub>2</sub> O <sub>14</sub>	1309.6	75	187-194	Dark
	octyloxybenzoyloxy) benzamide]					brown

# 2.3.10 Synthesis of N,N`-4,4`-biphenyl-bis[3``,4``,5``trihydroxybenzoic acid] and N,N`-1,4-phenyl-bis[3`,4`,5`trihydroxybenzoic acid] (20,21):

Gallic acid (0.003mol, 0.56g), *p*-phenyldiamine or benzidine (0.001mol) and a catalytic amount of *p*-toluensulfonic acid were dissolved in dioxane (5mL) in a distillation system. The mixture was heated at  $100^{\circ}$ C for 5 hour. The reaction mixture was allowed to reach room temperature and then was cooled by a water-ice bath to

give a precipitate that was filtered and washed with gently quantities of diethyl ether<sup>(36)</sup>.

# 2.3.11 Synthesis of N,N<sup>-4,4</sup>-biphenyl-bis[3<sup>,4</sup>,5<sup>,+</sup>,5<sup>,+</sup>-tri(4<sup>,+</sup>) alkoxybenzoyloxy)benzamide] and N,N<sup>-1,4</sup>-phenyl-bis[3<sup>,4</sup>,5<sup>,+</sup>,5<sup>,+</sup>tri(4<sup>,+</sup>-alkoxybenzyloxy)benzamide](22,23):

The same procedure used as in 2.3.1.4 using 4-alkoxybenzoyl chloride (0.18mol) and N,N<sup>-4</sup>,4<sup>-</sup>-biphenyl-bis[3<sup>,4</sup>,5<sup>-</sup>-trihydroxybenzoic acid] or N,N<sup>-1</sup>,4-phenyl-bis[3<sup>,4</sup>,5<sup>-</sup>-trihydroxybenzoic acid](0.003mol)<sup>(34)</sup>.

No.	Name of compound	Chemical	M.W.	Yield	m.p	color
		Formula	(g\mol)	%	°C	
22a	N,N <sup>-4,4</sup> - biphenyl-bis[3 <sup>,4</sup> ,5 <sup>,-</sup>	$C_{86}H_{80}N_2O_{20}$	1461.55	73	223-	Dark
	tri(4```-				229	brown
	propoxybenzyloxy)benzamide]					
22b	N,N`-4,4`-biphenyl-bis[3``,4``,5``-	$C_{92}H_{92}N_2O_{20}$	1545.7	60	215-	Dark
	tri(4```-				218	brown
	butoxybenzyloxy)benzamide]					
22c	N,N <sup>-4,4</sup> -biphenyl-bis[3 <sup>,4</sup> ,5 <sup>,-</sup>	$C_{98}H_{104}N_2O_{20}$	1629.57	65	210-	Dark
	tri(4```-				215	brown
	pentyloxybenzyloxy)benzamide]					
22d	N,N`-4,4`-biphenyl-bis[3``,4``,5``-	$C_{110}H_{128}N_2O_{20}$	1798.19	71	203-	Dark
	tri(4```-				209	brown
	heptoxybenzyloxy)benzamide]					
22e	N,N`-4,4`-biphenyl-bis[3``,4``,5``-	$C_{116}H_{140}N_2O_{20}$	1885.35	88	195-	Dark
	tri(4```-				201	brown
	octyloxybenzyloxy)benzamide]					

Table (2.6) Physical properties of the compounds [22a-e].

No.	Name of compound	Chemical	M.W.	Yield	m.p	color
		Formula	(g\mol)	%	°C	
23a	N,N`-1,4-phenyl-bis[3`,4`,5`-tri(4``-	$C_{80}H_{76}N_2O_{20}$	1385.40	75	219-	Dark
	propoxybenzoyloxy)benzamide]				226	brown
23b	N,N`-1,4-phenyl-bis[3`,4`,5`-tri(4``-	$C_{86}H_{88}N_2O_{20}$	1469.7	63	206-	Dark
	butoxybenzoyloxy)benzamide]				211	brown
23c	N,N <sup>-1</sup> ,4-phenyl-bis[3 <sup>,4</sup> ,5 <sup>-tri</sup> (4 <sup>-</sup> -	$C_{92}H_{100}N_2O_{20}$	1553.77	60	202-	Dark
	pentyloxybenzoyloxy)benzamide]				208	brown
23d	N,N`-1,4-phenyl-bis[3`,4`,5`-tri(4``-	$C_{104}H_{124}N_2O_{20}$	1722.1	65	193-	Dark
	heptoxybenzoyloxy)benzamide]				200	brown
23e	N,N <sup>-1</sup> ,4-phenyl-bis[3 <sup>,4</sup> ,5 <sup>-tri</sup> (4 <sup>,-</sup>	$C_{110}H_{136}N_2O_{20}$	1806.26	78	186-	Dark
	octyloxybenzoyloxy)benzamide]				190	brown

<i>Table (2.7) Physical properties of the compounds [23a-</i>	cal properties of the compounds [23a-e].
---	--



# CHAPTER THREE

**Results and Discussion** 



3.1 Synthesis of N,N`-4,4`-biphenyl-bis[3``,5``-dipropoxy benzamide] (10) , N,N`-1,4-phenyl-bis[3`,5`-dipropoxybenzamide] (11), N,N`-4,4`-biphenyl-bis[3``,4``,5``-tripropoxybenzamide] (12) and N,N`-1,4-phenyl-bis[3`,4`,5`-tripropoxybenzamide] (13)

The reaction's steps involve, firstly preparation of 3,5-dipropoxy and 3,4,5-tripropoxy benzoic acid as shown below scheme  $(3.1)^{(37)}$ :



Scheme 3.1 Mechanism steps for preparation of 3,5-dipropoxy and 3,4,5-tripropoxy benzoic acid.

The structures of prepared compounds were identified via FT-IR spectroscopy. Figure (3.1) shows the FT-IR spectrum of 3,5-dipropoxybenzoic acid (4) using KBr disc which showed the following characteristic absorption

bands: broad band at 3191 cm<sup>-1</sup> and 1720 cm<sup>-1</sup> that could be attributed to O - H stretching and carbonyl of carboxyl group respectively, and bands at 2914 and 2856 cm<sup>-1</sup> due to aliphatic C - H stretching of alkyl group, while the C = C stretching occurs at 1608 cm<sup>-1</sup>. While Figure (3.2) shows the FT-IR spectrum of 3,4,5-tripropoxybenzoic acid (5) which showed the following characteristic absorption bands: broad band at 3361 cm<sup>-1</sup> and 1716 cm<sup>-1</sup> that could be attributed to O - H stretching and carbonyl of carboxyl group respectively and bands at 2921 and 2873 cm<sup>-1</sup> due to aliphatic C - H stretching of alkyl group, while the C = C stretching occurs at 1595 cm<sup>-1</sup>.



Figure 3.1 FT-IR spectrum of 3,5-dipropoxybenzoic acid (4).



Figure 3.2 FT-IR spectrum of 3,4,5-tripropoxybenzoic acid (5).

Compounds (4) and (5) were refluxed with thionyl chloride to afford 3,5dipropyloxy and 3,4,5-tripropoxybenzoyl chloride (6) and (7) respectively, according to  $SN_i$  mechanism<sup>(38)</sup>as shown below scheme (3.2):



Scheme 3.2 Mechanism steps for preparation of 3,5-dipropoxy and 3,4,5-tripropoxybenzoyl chloride (6) and (7).

Figure (3.3) show the FT-IR spectrum of compound (6), which showed the disappearance of hydroxyl group stretching band and shifting the carbonyl group from 1720 to 1768 cm<sup>-1</sup> which is good evidence for preparation the desired compound.



Figure 3.3 FT-IR spectrum of 3,5-dipropoxybenzoyl chloride (6).

Reaction of compound (6) with benzidine (8) and 1,4-phenylenediamine (9) afford the preparation of compounds (10) and (11) respectively, according to tetrahedral mechanism<sup>(39)</sup>as shown below scheme (3.3):



Scheme 3.3 The synthetic pathway for compounds N,N`-1,4-phenyl-bis[3`,5`dipropoxybenzamide] (10).

The spectrum of compound (10) figure (3.4), shows the appearance of the N - H group stretching of amide at 3211. The spectrum also show bands at 3058, 2923, 2850, 1691, 1593, 1490 and 1182 due to Ar – H, C – H (aliph.), C=O (amide I), C = C, N - H bending (amide II), and C – O stretching respectively.

The spectrum of compound (11) figure (3.5), shows the appearance of the N - H group stretching of amide at 3186. The spectrum also show bands at 3055, 2918, 2850, 1685, 1569, 1502 and 1114 due to Ar – H, C – H (aliph.),C=O (amide I), C = C, N - H bending (amide II), and C – O stretching respectively.



Figure 3.4 FT-IR spectrum of N,N`-4,4`-biphenyl-bis[3``,5``-dipropoxybenzamide] (10).



Figure 3.5 FT-IR spectrum of N,N`-1,4-phenyl-bis[3`,5`-dipropoxybenzamide] (11).

The structure of compound (10) also characterized using <sup>1</sup>H-NMR spectroscopy. Figure (3.6) shows the <sup>1</sup>H-NMR spectrum of compound (10), the following characteristic chemical shifts (d<sub>6</sub>-DMSO, ppm) were appeared: A three pairs of doublets at  $\delta$ 7.08-8.94 could be attributed to the fourteen protons of the biphenyl and phenyl rings. The <sup>1</sup>HNMR also showed a broad two proton singlet at  $\delta$  9.50 which could be assigned to the amidic proton<sup>(40)</sup>. Twelve protons appeared as triplet at  $\delta$  0.9 – 1.0 that are attributed to –CH<sub>3</sub>, eight protons appeared as triplet at  $\delta$  2.8 – 2.9 which could be assigned to –O CH<sub>2</sub> group while the other – CH<sub>2</sub> group of propyl substituent appeared as multiplet at  $\delta$  1.4 – 1.8.





While the reaction of compound (7) with benzidine (8) and 1,4phenylenediamine (9) give compounds (12) and (13) respectively.

The spectrum of compound (12) figure (3.7), shows the appearance of the N - H group stretching of amide at 3305. The spectrum also show bands at 3049, 2916, 2846, 1695, 1612, 1496 and 1257 due to Ar – H, C – H (aliph.), C=O (amide I), C = C, N - H bending (amide II), and C – O stretching respectively. The spectrum of compound (13) figure (3.8) shows the appearance of the N - H group stretching of amide at 3321. The spectrum also show bands at 3058, 2923, 2850, 1691, 1616, 1498 and 1168 due to Ar – H, C – H (aliph.), C=O (amide I), C = C, N - H bending (amide II), and C – O stretching respectively.



Figure 3.7 FT-IR spectrum of N,N`-4,4`-biphenyl-bis[3``,4``,5``-tripropoxybenzamide] (12).



Figure 3.8 FT-IR spectrum of N,N`-1,4-phenyl-bis[3`,4`,5`-tripropoxybenzamide] (13).

The structure of compound (12) also characterized using <sup>1</sup>H-NMR spectroscopy. Figure (3.9) shows the <sup>1</sup>H-NMR spectrum of compound (12), the following characteristic chemical shifts (d<sub>6</sub>-Acetone, ppm) were appeared: A doublets leaning on each other at  $\delta$ 7.42-8.06 could be attributed to the twelve aromatic protons of the biphenyl and phenyl rings. The <sup>1</sup>H-NMR also showed a broad two proton singlet at  $\delta$  9.34 which could be assigned to the amidic proton. Eighteen protons appeared as triplet at  $\delta$  0.9 – 1.1 that are attributed to –CH<sub>3</sub>, twelve protons appeared as triplet at  $\delta$  1.9 – 2.1 which could be assigned to – OCH<sub>2</sub> group while the other – CH<sub>2</sub> group of propyl substituent appeared as multiplet at  $\delta$  1.3 – 1.4.







# 3.2 Synthesis of N,N`-4,4`-biphenyl-bis[3``,5``-di(4```-alkyloxy benzoyloxy) benzamide] (18) and N,N`-1,4-phenyl-bis[3`,5`-di(4``alkyloxybenzoyloxy) benzamide] (19)

The benzoylation of 3,5-dihydroxy benzoic acid with 4alkoxybenzoylchloride afford the preparation of 3,5-di(4<sup>-</sup>alkoxybenzoyloxy)benzoic acid (16)a-e.



Scheme 3.4 the synthetic pathway 3,5-di(4`-alkoxybenzoyloxy)benzoic acid (16)a-e

The FT-IR spectrum of compound (16)c figure (3.10) shows the appearance of O – H stretching band of carboxyl group at 3388 cm<sup>-1</sup> and the appearance of bands at 3066, 2958, 2871, 1735, 1676, 1596, 1242 and 1162 due to Ar – H, C – H aliph., C = O (ester), C = O (acid), C – O – C (asymm. And symm.) respectively. Table 3-1 show the FT-IR bands value for compounds (16)a-e.



Figure 3.10 FT-IR spectrum of 3,5-di(4`-pentoxybenzoyloxy)benzoic acid (16)c.



Figure 3.11 FT-IR spectrum of 3,5-di(4<sup>-</sup>-propylbenzoyloxy)benzoic acid (16)a.



Figure 3.12 FT-IR spectrum of 3,5-di(4`-octyloxybenzoyloxy)benzoic acid (16)e.

Comp.	Alkyl	$\nu O - H$	ν C – H	ν C – H	v C = O	v C = O	v C - O - C
No.	group		Arom.	Aliph.	ester	acid	
16a	n-propyl	3366	3056	2931	1738	1681	1249 &
				2844			1166
16b	n-butyl	3421	3059	2962	1746	1691	1263 &
				2873			1155
16c	n-pentyl	3388	3066	2958	1735	1676	1242 &
				2871			1162
16d	n-heptyl	3398	3051	2923	1741	1701	1252 &
				2854			1122
16e	n-octyl	3378	3062	2942	1738	1697	1261 &
				2865			1168

Table (3.1) Characteristic FT-IR absorption bands of synthesizes compounds (16)a-e.

Treatment of compound (16)a-e with thionyl chloride produce 3,5-di(4<sup>-</sup> alkyloxybenzoyloxy)benzoylchloride (17)a-e, which react firstly with benzidine

to produce  $N,N^-4,4^-$ -biphenyl-bis $[3^{,5^-}-di(4^{,-}-alkoxybenzoyloxy))$ benzamide] (18)a-e, and secondly with 1,4-phenylenediamine to give  $N,N^-1,4$ phenyl-bis $[3^,5^-di(4^{,-}-alkyloxybenzoyloxy))$  benzamide] (19)a-e. The structure of these compounds was elucidated on the basis of elemental analysis, FT-IR and <sup>1</sup>H-NMR spectral data.

The FT-IR spectrum of compound (18)c figure (3.13) shows the appearance of N– H stretching band of amide group at 3230 cm<sup>-1</sup> and the appearance of bands at 3062, 2952, 2860, 1728, 1677, 1600, 1251 and 1164 due to Ar – H, C – H aliph., C = O (ester), C = O (amide), C = C, C – O – C (asymm. And symm.) respectively. Table 3.2 show the FT-IR bands value for compounds (18)a-e. While the value of elemental analysis show in table (3.3).



Figure 3.13 FT-IR spectrum of N,N`-4,4`-biphenyl-bis[3``,5``-di(4```-pentoxybenzoyloxy) benzamide] (18)c.



Figure 3.14 FT-IR spectrum of N,N<sup>-4</sup>,4<sup>-</sup>-biphenyl-bis[3<sup>-</sup>,5<sup>-</sup>-di(4<sup>-</sup>) heptoxybenzoyloxy)benzamide] (18)d.

<sup>1</sup>H-NMR spectrum of compound (18)a, figure (3.15) showed the following characteristics chemical shifts (d<sub>6</sub>-DMSO as a solvent, ppm): A doublets at  $\delta$  7.19-8.15 could be attributed to the aromatic protons of the biphenyl and phenyl rings. The <sup>1</sup>H-NMR also showed two proton singlet at  $\delta$  9.06 which could be assigned to the amidic proton. Twelve protons appeared as triplet at  $\delta$  0.93 – 1.18 that are attributed to –CH<sub>3</sub>, eight protons appeared as triplet at  $\delta$  2.82 – 2.95 which could be assigned to – OCH<sub>2</sub> group while the other – CH<sub>2</sub> group of propyl substituent appeared as multiplet at  $\delta$  1.54 – 1.79.



Figure 3.15 <sup>1</sup>H-NMR spectrum of N, N -4,4 - biphenyl-bis[3, 5 -di(4) - propylbenzoyloxy) benzamide] (18)a.

Comp.	υ C-H	υ C=O	υ C=O	υ C=C	υ C – O	υ N –H
No.	Aliphatic	Amide	Ester	aromatic		Amide
18a	2951	1680	1738	1600	1254	3287
	2860				1158	
18b	2932	1702	1741	1602	1254	3231
	2865					
18c	2952	1677	1728	1600	1251	3230
	2860				1164	
18d	2987	1698	1739	1597	1247	3214
	2877				1164	
18e	2955	1681	1739	1598	1225	3220

Table (3.2) Characteristic FT-IR absorption bands (cm<sup>-1</sup>) of synthesized compounds (18)ae.

Table (3.3) Elemental Analysis (CHN) for compounds (18)a,c,d.

Comp. No	Formula	%	%C %H		%N		
		Calc.	Found	Calc.	Found	Calc.	Found
<b>18</b> a	$C_{66}H_{60}N_2O_{14}$	71.73	72.03	5.43	5.48	2.53	2.48
18c	C <sub>74</sub> H <sub>76</sub> N <sub>2</sub> O <sub>14</sub>	73.02	72.98	6.25	6.14	2.30	2.29
18d	$C_{82}H_{92}N_2O_{14}$	74.09	74.21	6.92	6.88	2.10	2.09

The FT-IR spectrum of compound (19) a figure (3.16) show the disappearance of two absorption band due to (-NH<sub>2</sub>) str. of amine with appearance band at (3291) cm<sup>-1</sup> due to amide N – H stretching. Moreover, the compound exhibit significant stretching bands near the region (2974, 2862, 1728, 1676, 1600, 1251 and 1166) cm<sup>-1</sup>, these indicated the presence of (C – H (aliph.), C = O (ester), C = O (amide) C = C, C – O – C) groups. Table (3.4) shows the characteristic FT-IR absorption bands for compounds (19)a-e, while table (3.5) shows the (CHNS) value for some of them.

Comp.	υ C-H	υ C=O	υ C=O	υ C=C	υ C – O	υ N –H
No.	Aliphatic	Amide	Ester	aromatic		Amide
19a	2974	1676	1728	1600	1251	3291
	2862				1166	
19b	2850	1682	1732	1573	1272	3188
19c	2987	1679	1739	1597	1259	3110
	2885				1100	
19d	2886	1673	1729	1606	1190	3205
19e	2923	1685	1734	1605	1220	3267

Table (3.4) Characteristic FT-IR absorption bands (cm<sup>-1</sup>) of synthesized compounds (19)a-e.

Table (3.5) Elemental Analysis (CHN) for compounds (19)a, e.

Comp	Formula	%C		% H		%N	
• 1 (0		Calc.	Found	Calc.	Found	Calc.	Found
19a	$C_{60}H_{56}N_2O_{14}$	70.03	69.96	5.44	4.99	2.72	2.74
19e	C80H96N2O14	73.39	73.24	7.33	7.28	2.14	2.16



Figure 3.16 FT-IR spectrum of N,N`-1,4-phenyl-bis[3`,5`-di(4``-propoy benzoyloxy)benzamide] (19)a.



Figure 3.17 FT-IR spectrum of N,N`-1,4-phenyl-bis[3`,5`-di(4``-propoyl benzoyloxy)benzamide] (19)c.

Chapter Three

<sup>1</sup>H-NMR spectrum of compound (19)b, figure (3.18) showed the following characteristics chemical shifts (DMSO as a solvent):  $\delta$  6.64-8.15 m, (aromatic protons);  $\delta$  9.64 ( amidic –NH);  $\delta$  0.96 t (–CH<sub>3</sub>);  $\delta$  1.75 m (–CH<sub>2</sub>–CH<sub>2</sub>);  $\delta$  3.94 t (–OCH<sub>2</sub>).



47

Figure 3.18  $^{1}$ H-NMR spectrum of N,N'-1,4-phenyl-bis[3',5'-di(4''-butoxybenzoyloxy) benzamide](19)b.

3.3 Synthesis of N,N<sup>-4</sup>,4<sup>-biphenyl-bis[3<sup>,4</sup>,5<sup>-tri(4<sup>,</sup>-alkyloxy benzoyloxy) benzamide] (22) and N,N<sup>-1</sup>,4-phenyl-bis[3<sup>,4</sup>,5<sup>-tri(4<sup>,</sup>-alkyloxybenzoyloxy) benzamide] (23)</sup></sup></sup>

The synthetic steps involve the preparation of N,N<sup>-4,4<sup>-</sup></sup>-biphenylbis[3<sup>,4<sup>,5</sup></sup>,5<sup>,-tri</sup>(hydroxy)benzamide] (20) and N,N<sup>-1,4</sup>-phenyl-bis[3<sup>,4<sup>,5</sup></sup>,5<sup>-tri</sup> (hydroxy) benzamide] (21) by the reaction gallic acid with benzidine and 1,4phenylenediamine respectively, using *p*-toluenesulphonic acid as catalyst and dioxane as solvent<sup>(41)</sup>.



Scheme 3.5 the synthetic pathway N,N`-4,4`-biphenyl-bis[3``,4``,5``-tri(hydroxy)benzamide] (20) and N,N`-1,4-phenyl-bis[3`,4`,5`-tri (hydroxy) benzamide] (21).

The reaction of compounds (20) and (21) with 4-alkoxybenzoylchloride afford the synthesis of  $N,N^-4,4^-biphenyl-bis[3^-,4^-,5^--tri(4^-)alkyloxybenzoylox)$  benzamide] (22)a-e and  $N,N^-1,4$ -phenyl-bis[3^-,4^-,5^-tri(4^-)alkyloxybenzoylox) benzamide] (23)a-e. The structures of the synthesized compounds were identified by FT-IR, <sup>1</sup>H-NMR and elemental analysis (CHNS).

The FT-IR spectrum of compound (22)e figure (3.19) show the disappearance of hydroxyl group stretching with the appearance of bands at 3122, 3056, 2925, 2852, 1745, 1676, 1604, 1249 and 1164 cm<sup>-1</sup> due to (N – H, C – H (aromatic), C – H (aliphatic), C = O (ester), C = O (amide) C = C, C – O – C ) groups. Tables (3.6) and (3.7) show the characteristic FT-IR absorption bands and elemental analysis for compounds (22) a-e respectively.



Figure 3.19 FT-IR spectrum of N,N`-4,4`-biphenyl-bis[3``,4``,5``-tri(4```-octybenzoyloxy) benzamide] (22)e.



heptoxybenzoyloxy) benzamide] (22)d.

<sup>1</sup>H-NMR spectrum of compound (22)a, figure (3.21) showed the following characteristics chemical shifts (d<sub>6</sub>-DMSO as a solvent, ppm): A doublets leaning on each other at  $\delta$  7.7-8.1 could be attributed to the aromatic protons of the biphenyl and phenyl rings. The <sup>1</sup>H-NMR also showed two proton singlet at  $\delta$  9.12 which could be assigned to the amidic proton. Eighteen protons appeared as triplet at  $\delta$  0.9 – 1.0 that are attributed to –CH<sub>3</sub>, twelve protons appeared as triplet at  $\delta$  2.8 – 2.9 which could be assigned to – OCH<sub>2</sub> group attached by phenyl while the other – CH<sub>2</sub> group of propyl substituent appeared as multiplet at  $\delta$  1.6 – 1.7.


Comp. No	Formula	%C		% H		%N	
		Calc.	Found	Calc.	Found	Calc.	Found
22a	$C_{86}H_{80}N_2O_{20}$	70.58	71.03	5.60	5.87	1.91	2.02
22b	$C_{92}H_{92}N_2O_{20}$	71.41	69.98	6.080	5.91	1.81	1.79

Table (3.6) The Elemental Analysis (CHN) for compounds 22a,b.

Table (3.7) Characteristic FT-IR absorption bands (cm<sup>-1</sup>) of synthesized compounds (22)a-e.

Comp.	υ C-H	υ C=O	υ C=O	υ C=C	υ C – O	υ N –H
No.	Aliphatic	Amide	Ester	aromatic		Amide
22a	2934	1685	1746	1591	1286	3324
	2866				1172	
22b	2953	1704	1732	1602	1253	3288
	2869				1168	
22c	2931	1703	1732	1598	1246	3231
	2828				1136	
22d	2921	1677	1742	1589	1294	3287
	2831				1166	
22e	2925	1676	1745	1604	1249	3122
	2852				1164	

Compounds (23)a-e were synthesized through the reaction of N,N<sup>-1,4-</sup> phenyl-bis[3<sup>,4</sup>,5<sup>-</sup>-tri (hydroxy) benzenamide] with six equivalent moles of the appropriate 4- alkoxybenzoyl chloride in dry pyridine. Table (3.8) show the elemental analysis of compounds (23)b, c. The structures of the synthesized compounds were identified by FT-IR, <sup>1</sup>H-NMR and elemental analysis (CHNS). The FT-IR spectrum of compound (23)d figure (3.22) shows the disappearance of two absorption band due to (-NH<sub>2</sub>) str. of amine with appearance bands near the region (3319, 2947, 2858, 1728, 1685, 1600, 1249) cm<sup>-1</sup>, these indicated the

52

presence of (N – H, C – H, C = O (ester), C = O (amide) C = C, C – O) groups. Table (3.9) shows the characteristic FT-IR absorption bands for compounds (23)a-e. <sup>1</sup>H-NMR spectrum of compound (23)b, figure (3.24) showed the following characteristics chemical shifts (DMSO as a solvent):  $\delta$  7.2-7.9 m, (aromatic);  $\delta$  9.5 s (–NH);  $\delta$  4.99-5.03 t(–OCH<sub>2</sub>)  $\delta$  0.99 t (–CH<sub>3</sub>);  $\delta$  1.99 m (CH<sub>2</sub>–CH<sub>2</sub>).

 Table (3.8) The Elemental Analysis (CHN) for compounds [23] a,c.

Comp. No	Formula	%C		% H		%N	
110		Calc.	Found	Calc.	Found	Calc.	Found
23b	$C_{86}H_{88}N_2O_{20}$	70.29	69.71	5.99	5.61	1.90	2.02
23c	$C_{92}H_{100}N_2O_{20}$	71.13	70.88	6.44	6.74	1.80	1.84

Table (3.9) Characteristic FT-IR absorption bands (cm<sup>-1</sup>) of synthesized compounds[23]a-e.

Comp.	υ C-H	υ C=O	υ C=O	υ C=C	υ C – O	υ N –H
No.	Aliphatic	Amide	Ester	aromatic		Amide
23a	2886	1669	1741	1602	1259	3206
23b	2841	1678	1738	1600	1245	3398
23c	2871	1679	1740	1602	1255	3326
23d	2947 2858	1685	1728	1600	1249	3319
23e	2987 2877	1616	1734	1594	1253	3112



Figure 3.22 FT-IR spectrum of N,N`-1,4-phenyl-bis[3`,4`,5`-tri(4``-octyloxybenzoyloxy) benzamide](23)d.



Figure 3.23 FT-IR spectrum of N,N<sup>-1</sup>,4-phenyl-bis[3<sup>,4</sup>,5<sup>-tri</sup>(4<sup>,-</sup> octyloxybenzoyloxy)benzamide](23)e.



#### 3.4 Thermotropic Liquid Crystalline Properties of synthesized compounds

Bis swallow compound containing rigid core (phenyl or biphenyl) have been regarded as the most suitable structure to obtained mesogenic properties<sup>(42)</sup>. Most of known thermotropic liquid crystals are calamitic structurally<sup>(43)</sup>. A calamitic mesogen molecule consists of a core (e.g. aromatic rings), terminal chains (e. g. alkyl or alkoxy group) and lateral substituents.

# **3.4.1 Phase Transitions**

The phase transition temperatures were determined using differential scanning calorimetry (DSC). The DSC thermogram of compounds 10,11,12 and 13 show two peaks represent the crystal – crystal and crystal – isotroupic transition so it did not show and mesomorphic properties, The absence of mesomorphicity of compounds 10,11,12 and 13 might be due to the length of alkoxy group which is less than half the length of the molecules <sup>(44)</sup> figures (3.25)a-d below.



Figure 3.25 Differential scanning thermogram of compounds 10, 11, 12 and 13 as a function of temperature for the second heating and cooling cycles (at scan rate10 °C min<sup>-1</sup>).

The DSC thermograms of compounds (18)a-e are shown in figure (3.26), two exothermic peaks were found on cooling from the isotropic liquid.

On heating to the isotropic liquid, a sharp melting peak appeared as shown in table 3.10. All the synthesized compounds show nematic mesophases.

Comp. No.	Melting point °C	Transition
<b>18</b> a	100 - 105 105 - 162	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$
18b	143 - 145 145 - 157	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$
18c	112 - 115 115 - 129	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$
18d	$80 - 90 \\ 90 - 140$	$\begin{array}{c} C \rightarrow N \\ N \rightarrow I \end{array}$
18e	196 - 206 206 - 214	$\begin{array}{c} C \rightarrow N \\ N \rightarrow I \end{array}$

 Table (3.10) Melting points and type of transition for compounds (18)a-e.





Figure 3.26 Differential scanning thermogram of compound 18a and 18d as a function of temperature for the second heating and cooling cycles (at scan rate 10 °C min<sup>-1</sup>).

The DSC thermograms of compounds (19)a-e are shown in figure (3.27)a,c, two exothermic peaks were found on cooling from the isotropic liquid for the synthesized compounds.

On heating to the isotropic liquid, a sharp melting peak appeared as shown in table 3.11. Compounds (19)a-e show nematic mesophases.

Comp. No.	Melting point°C	Transition
19a	110 - 120 120 - 160	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$
19b	106 - 111 111 - 141	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$
<b>19c</b>	135 - 140 140 - 165	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$
19d	154 - 158 158 - 178	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$
<b>19</b> e	147 - 150 150 - 184	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$

Table (3.11) Melting points and type of transition for compounds (19)a-e.

C = Crystal; N = Nematic



Figure 3.27 Differential scanning thermogram of compound 19a and 19c as a function of temperature for the second heating and cooling cycles (at scan rate 10 °C min<sup>-1</sup>).

Compounds (22)a-e and (23)a-e also examined by DSC as shown in figures (3.28) and figures (3.24), which shows two transitions, the temperature at the maximum of the first transition peaks was chosen as the actual transition temperature, Crystal to Nematic ( $C \rightarrow N$ ) and the second one is the transition from Nematic to Isotropic ( $N \rightarrow I$ ), as show in table (3.12) and (3.13).

Comp. No.	Melting point°C	Transition
22a	123 –125 125 – 139	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$
22b	115 - 118 118 - 128	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$
22c	110 - 115 115 - 143	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$
22d	138 - 141 141 - 165	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$
22e	$105 - 108 \\ 108 - 137$	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$

Table (3.12) Melting points and type of transition for compounds (22)a-e.

C = Crystal; N = Nematic



Figure 3.28 Differential scanning thermogram of compound 22d as a function of temperature for the second heating and cooling cycles (at scan rate 10 °C min<sup>-1</sup>).

Table	(3.13)	Melting points	and type of	<sup>f</sup> transition for	compounds	(23)a-e
	(00)				e o mp o mmo	(==)

Comp. No.	Melting point°C	Transition
23a	$\begin{array}{c} 219-220 \\ 220-257 \end{array}$	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$
23b	$\begin{array}{c} 206-210 \\ 210-234 \end{array}$	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$
23c	$\begin{array}{c} 202-205\\ 205-225\end{array}$	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$
23d	193 – 195 195 – 240	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$
23e	250 - 254 254 - 272	$\begin{array}{c} C \longrightarrow N \\ N \longrightarrow I \end{array}$

#### C = Crystal; N = Nematic



Figure 3.29 Differential scanning thermogram of compound 23e as a function of temperature for the second heating and cooling cycles (at scan rate 10 °C min<sup>-1</sup>).

#### **3.4.2** Phase structure

The phase structures were determined by polarizing optical microscope (POM), Microscopic observations of compounds 10, 11, 12 and 13, revealed that these compounds did not show liquid crystal properties.

The potential mesogenic properties of (18)a-e have been checked with a polarizing microscope equipped with a heating stage and a single melting point has been noticed at 196 – 261 °C. This behaviour may be explained by the flexibility of molecule  $^{(35)}$ .

Terminal substituents play a significant role in promoting liquid crystalline properties in a mesogen <sup>(45)</sup>.

Examination of compounds (19)a-e by means of hot stage polarizing microscope Individual thermal microscopic observation of this series revealed that these compounds showed a Spherical droplets nematic phase, figure (3.30).

The presence of a biphenyl ring into the principle structure of compound (18)a-e could cause considerable changes of polarity, polarizability and geometry of the molecules and influenced the type and the phase transition temperature of the mesophases<sup>(46)</sup>.



Figure 3.30 Spherical droplets nematic phase of compound 19c at 174 °C (magnification  $10 \times 10$ ).

Liquid crystalline properties of compound (22)a-e also were examined by means of hot stage polarizing microscope which showed nematic mesophase, Figure (3.31).



Figure 3.31 Schlieren texture of the nematic phase of compound 22d at 206°C (magnification 10×10).



Figure 3.32 Schlieren texture of the nematic phase of compound 23c at  $206^{\circ}C$  (magnification  $10 \times 10$ ).

## 3.5 Photoluminesce Spectra

Measurement of Luminescence in conjugated compounds are important both for understanding the nature of the excited states, and the operation of electroluminescent devices <sup>(47)</sup>. The photoluminesce measurements have been studied using the fluorescence spectrometer in the range (200-900 nm).

Figure 3.33 shows the emission spectrum for the Xe lamp used to excite the studied samples.



Figure 3.33 The emission spectrum for the Xe lamp used to excite the studied samples.

The comparison between the spectra of synthesized (18)a, (19)c, (22)d and (23)c as shown in figures 3.34 - 3.37, we observe that compound (22)d highly absorb at the UV and blue range. There is high emission spectrum at the visible range between (480-800 nm). While the absorption edge for the same sample end at 585 nm.



Figure 3.34 The PL spectrum for compound (18)a.



Figure 3.35 The PL spectrum for compound (19)c.



Figure 3.36 The PL spectrum for compound (22)d.



Figure 3.37 The PL spectrum for compound (23)c.



# REFERENCES



# References

- Den K. and Shin T. Wu: "Fundamentals of Liquid Crystal Devices", John Wiley & Sons Ltd, 1-2, 2006.
- 2- Suzuki and Koide N.: "Synthesis and Characterization of Biphenylethynylbenzene Type discotic Liquid Crystal", vol.364, 1, 635-645, 2001.
- 3- Lu G. Chen: "Thermo-Optical Properties of Polymer Dispersed Liquid Crystals, Science, Engineering and Technology", Portfolio RMIT University, 4-5, 2007.
- 4- Gopal R. and Deepak J.: "Recent Characterization and applicability of Polymorphism: Liquid Crystal", International Journal of Pharmaceutical Sciences Review and Research, Vol 4, Issue 2, 129-130, 2010.
- 5- Puttewar T., Shinde A. and Patil R.: "a review on liquid crystals a novel drug delivery system", Shankarrao Ursal College of Pharmaceutical Sciences and Research Centre, Vol 4, 571-572, 2014.
- 6- Denis A.: "Introduction to liquid crystals", International Max Planck Research School, 1-2, 2006.
- 7- Iam-choon K.: "Liquid Crystals", Wiley-interscience, 2nd edition, 1-5, 2007.
- 8- Fadi I.: "Synthesis of smectic and discotic liquid crystals derivatives by flow injection system", International Journal of Nanotechnology and Application, Vol. 5, Issue 4, 9-10, 2015.
- 9- Bin W.: "Organic pi-stacking Semiconducting Material: Design, Synthesis and the Analysis of Structure and Properties", cuny Academic Works, 10-11, 2014.

- Ermakov S., Beletskii A., Eismont O., Nikolaev V.: "Liquid Crystals in Biotribology", Springer International Publishing Switzerland, 37-41, 2016.
- Jiang-Gen A., Saba H., Yong Y., Min X. and Yongsong L.:
   "Characterization of liquid crystals : a literature review", School of Science, Zhejiang Sci-Tech University, 44, 398-406, 2016.
- 12- Bong S. HAO: "synthesis and characterization of schiff base liquid crystals possessing dialkylamino terminal unit", Bachelor of Science (Hons) Chemistry, 22-25, 2011.
- Sackmann H.: "Plenary Lecture. Smectic liquid crystals: A historical review, liquid crystals", Vol. 5, Issue 1, 43-55, 1989.
- Maiti S.: "Liquid-Crystal and Nano-Crystal Technology for Solubilization of Poorly Water Soluble Drugs", Journal of PharmaSciTech, 2(1):1-4, 2012.
- 15- Karan T.: "formation of lyotropic liquid crystals through the selfassembly of bile acid building blocks", B.E. University of Pune, 5-6, 2007.
- James A., Jamie A., Andrew L. Mac K. and Elysse G., "Asymmetric synthesis of a highly soluble 'trimeric' analogue of the chiral nematic liquid crystal twistagent Merck S1011", Liquid Crystals, vol 37 ,37–43, 2010.
- Sahara M., Yano S., Ikemoto K. and Maejima Z.: "Liquid Crystal", 15, 929-931, 1993.
- 18- Satyendra K.: "liquid crystals experimental study of physical properties and phase transitions", Cambridge university press, 5-9, 2001.
- Ying Z. : "cholesteric liquid crystal photonic crystal laser and photonic devices", University of Central Florida Orlando, Florida, 5-8, 2008.

- 20- Prajakta P., Maya T.: "Liquid Crystalline Phase & its Pharma Applications", International Journal of Pharma Research & Review, 2(12):40-52, 2013.
- Parsley M. : "Hallcrest Handbook of Thermochromic Liquid Crystal Technology", Hall crest product and information Illinois U.S.A., 21-22, 1991.
- 22- Baron M. and Stepto R.: "definitions of basic terms relating to Polymer liquid crystals", International union for pure and applied chemistry, Vol. 74, No. 3,493–509, 2002.
- Guangyuan S., Yanhui Z., Eunice S. Ping and Yan J. Liu: "Liquid-Crystal-Enabled Active Plasmonics: A Review, Materials", 1296-1317, 2014.
- S. M. Kelly, M. O'Neill, : "Handbook of Advanced Electronic and Photonic Materials and Devices", Vol. 72000 by Academic Press,27-28, 2002.
- 25- . Kasi V., Murthy Y. and Kondalarao T.: "Mesophase behaviour of 1, 3-diacyloxy and 1,4-diacyloxy esters", Der Pharma Chemica, 8(2):154-161, 2016.
- 26- Christian A. G. N. Montalbetti and Virginie Falque, "Amide bond formation and peptide coupling", Tetrahedron 61, 10827–10852, (2005).
- 27- Nasreen R., Mohammad M. and Ahmed A.: "Schiff Base liquid Crystals with Terminal Alkoxy Group Synthesis and Thermotropic Properties", Journal of Al-Nahrain University, Vol.17 (2), 2-3, 2014.
- 28- Kyung T. Kang, Jeong T. Kim, Ryeo Y. Hwang, Song J.Park, Seng K. Lee, Jong G. Lee and Yong B. Ki, "synthesis and mesomorphic properties of New Achiral Liquid Crystals with 3-Alkoxy-2-(alkoxymet hyl)-1-propoxy Swallow-Tails", Bull. Korean Chem. Soc., Vol. 28, No. 11, 1939-1943, 2007.

- 29- David D. : "synthesis and mesogenic properties of liquid crystals with bent core-tail substitution geometry", Kent State University, 125-126, 2013.
- 30- Weissflog W., Pelz G., Letk I., Max P. and Martin L. : "Crystalline -Smectic C - Cubic - Isotropic - Nematic - Isotropic polymorphism: synthesis and unexpected behaviour of a new series of double-swallowtailed mesogens, Mol. Cryst. Liq. Cryst. ", Vol. 260, 157-170, 1995.
- 31- Vocal A.: "A Text Book of Practical Organic Chemistry", Longman, London, 5th edition,562-561, 1998.
- 32- Johnson J. and Port (Eds) R. : "Liquid Crystals and Ordered Fluids", Plenum Press, New York, Vol. 1, 311-337, 1970.
- 33- Doshi A. A. and patel V. R.:" Study of an azoester novel homologous series: 4-[4'-n-alkoxy benzoyloxy]-3- methoxy phenyl azo- 3"- chloro benzenes ", Pharma Chemica, 4(3), 1174-1179, 2012.
- 34- Chauhan M., Bhoi D., Machhar M., Solanki D. and Dhaval S. : "Synthesis, characterization and mesomorphic properties of azoester mesogens: 4-nalkoxybenzoic acid 4-[3-(benzylidene-amino)-phenylazo]phenyl ester ", PharmaChemica, 2(4), 30-37, 2010.
- 35- Ali H. and Nasreen J.: "synthesis and characterization of new discotic liquid crystals compounds", ijrpc, 5(4), 527-535, 2015.
- 36- Rivero-Buceta E., Carrero : "Linear and branched alkyl-esters and amides of gallic acid and other (mono-, di- and tri-) hydroxy benzoyl derivatives as promising anti-HCV inhibitors", Eur J Med Chem., 2015.
- 37- Michael B. Smith and Jerry M.: "March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", New York, Wiley-Interscience, 6th edition, 426-427, 2007.
- 38- Clayden J., Greeves N. and Warren S. : "Organic Chemistry", New York, Oxford University Press, 2nd edition, 2001.

- 39- Paula Y. Bruice: "Organic Chemistry", university of California, santa Barbara, 6th edition, 721-723, 2006.
- 40- Robert M., Francis X., David J., David L. : "Spectrometric Identification of Organic Compounds", Wiley, 8th Edition, 2015.
- 41- BE´ nyei G., Jalsovszky I., Slugovc C., Trimmel G., Pelzl G., Vajda
  A., E´ber N. and Fodor-csorba K.: "Liquid Crystals", 32 (2), 197–205, 2005.
- 42- Rahman M., Salisu A., Silong S., Lutfor M. and Ayub M. : "Nematic Calamitic Bisazobenzene Liquid Crystal: Synthesis and Mesomorphic Properties of 1-Methoxybutyloxy-4<sup>-</sup>(4- Phenylazo)Azobenzene", Asian Journal of Applied Sciences,2(2), 177-183, 2009.
- 43- Liliana C., Csunderlik C. And Otilia C., Chem. Bull, 50(64), 1-2, 2005.
- 44- Nasreen J., Zainab H.: "the preparation and liquid crystalline properties of some homologues series of 1, 2, 4,-oxadiazole derivatives ", Ir. J. of Sci.51 (2), 220-227, 2010.
- 45- Nisreen H., Jumbad H., Ammar H. and Nasreen J.: "Synthesis and Liquid Crystalline Behavior of New Amides and Esters Containing 7, 1-Thiazole Ring", Al-Nahra. Univ. 71(4), 67-75, 2014.
- 46- Dunmur D., Fukuda A. and Luckhurst G.: "Praefcke K. in Physical Properties of Liquid Crystals. Nematics", ed. INSPEC, London, 17–35 2001.
- 47- Samuel D., Rumbles G and Collison C., Phys. Rev., 52(16), 573-576,
  1995.

### الملخص

تتضمن الدراسة تحضير و تشخيص مركبات بلورية سائلة مشتقة من ثنائي وثلاثي –هيدروكسي حامض البنزويك تتميز بنهايات ثنائية منتفخة و المسمى

 $N,N^-1,4$ -phenyl-bis $[3^,5^-disubstitutedbenzamide], <math>N,N^-4,4^-biphenly-bis[3^,5^-disubstitutedbenzamide], <math>N,N'-1,4$ -phenyl-bis $[3^,4^,5^-trisubstitutedbenzamide]$  and  $N,N^-4,4^-biphenyl-bis[3^,4^,5^-trisubstitutedbenzamide]$  benzamide]

و تم التحضير وفقا للمخططات الاتية:



مخطط:1



مخطط:2



مخطط: 3

المركبات المحضرة تم تشخيصها باستخدام طيف الأشعة تحت الحمراء FTIR وطيف الرنين المغناطيسي النووي HNMR<sup>I</sup> و تحليل العناصر (CHNS) لبعض منها. تم دراسة الصفات البلورية السائلة للمركبات المحضرة و تأثير النهايات الطرفية على ظهور الاطوارو استقرارها باستخدام مجهر الضوء المستقطب المزود بمسخن حراري وكذلك مسعر المسح التفاضلي. أظهرت المركبات المحضرة خصائص التلالئ الفوتوني في محاليل عضوية وفي درجة حرارة الغرفة، تراوحت حزمة التفاور 400 نانومتر. جمهورية العراق

وزارة التعليم العالي والبحث العلمي

كلية العلوم /جامعة النهرين

قسم الكيمياء



تحضير و تشخيص مشتقات البنزمايد ثنائية و ثلاثية التعويض كميز وجينات ذات نهايات منتفخة







