

# Preparation of Series Schiff Bases

Dr. Karim Jaber S

Assist Prof., Department of Chemistry, Faculty of Science, Iraq,  
(to corresponding : karee2000@gmail.com).

**Abstract:** This paper involved preparation of two types of imine compounds differ in the type of terminal group, where one of them has a terminal carboxyl group COOH while the other contains methoxy OCH<sub>3</sub> as a terminal group. In the first part of this research it was Identification by spectroscopy methods using infrared IR and nuclear magnetic resonance H NMR spectrum, besides elemental analysis shows the exact chemical structure of the expected synthesized compounds.

In the second part was the study of liquid-crystalline behavior by polarized optical microscopy POM and differential scanning calorimetry DSC that showed a liquid crystal phase in the compounds that has odd number of carbon atoms in the terminal chain compounds in the first series, while the second series compounds showed liquid crystal phase in the compounds that containing even number of atoms of carbon in the terminal chain.

**Keywords:** heat, nod

## I. INTRODUCTION

heneazomet are a new phases of mater add to the three well-known phases (solid, liquid and gas)[1]. The differences between these three well-known states can be attributed to the temperature of the substance. Temperature is a measure of the randomness of the molecules and therefore the higher of temperature is the less order they exist. Increasing temperature will cause the transition from a solid to a liquid and then to a gas. However, Many materials exhibit more than a single transition when passing from solid to liquid, which proves the presence of one or more intermediate phases[2]. The new phases have mechanical, optical and structural properties between those of crystalline solid and the corresponding isotropic liquid. These phases are referred to as liquid crystalline phases[3,4].

Thermotropic liquid crystals is one of two types of liquid crystals (and the second is called lyotropic), Most thermotropic liquid crystals are rod-like molecules having a rigid core composed of two or more aromatic rings and one or more flexible terminal chains.

The liquid crystal mesogen must contain a side-chain to give a linear that required to the liquid crystalline behavior. Schiff base (also known as imine CH=N) is a linking group used to connect between core groups. It has been received overwhelming response in liquid crystals research ever since in 1970 where Kelker discovered the 4-methoxybenzylidene-

4'-butylaniline (MBBA) which exhibit nematic phase at room temperature.

In this our studies, Schiff base and alkyloxy terminal moieties are incorporated into a new series of homologous compounds with two different group in the other side of chain,

4-(-alkoxybenzylideneamino)benzoic acid and 4-methoxy-N-(4-alkoxybenzylidene)aniline.

## II. EXPERIMENTAL

### Preparation of N-(4-hydroxyphenyl) acetamide

1- 18.3 mL of concentration hydrochloric acid and, (0.22mol, 23.98 gm) of para-amino phenol were introduced in a beaker containing 500ml of distilled water. The mixture was stirred until the amine completely passes in to solution.

2- To the resulting solution 25.6mL of acetic anhydride with (three drops of H<sub>2</sub>SO<sub>4</sub>acidconcentration) were added and stirred and then immediately was poured in a solution of (33gm, 0.402mol) of crystallized sodium acetate in 100mL of water. The solution was stirred vigorously and cooled in ice.

3- The N-(4-hydroxyphenyl) acetamide was filtered with suction washed with a little distilled water, and dried upon filter paper in air melting point was (169-170) C°. [5,6]

### Preparation of N-Alkali bromides

1- In a round bottomed flask equipped with a separation funnel and a condenser set downward for distillation, (71ml) of HBr acid (48%) and (16.5ml) of concentration H<sub>2</sub>SO<sub>4</sub>acid drop wise was added with stirring.

2- After cooling(0.5mol) of appropriate alcohol was added in portions (the end of the condenser was connected to an adapter dipping in to water contained in a 250ml flask, the later was surrounded by ice) then (2.5ml) of concentration H<sub>2</sub>SO<sub>4</sub> acid was introduced gradually through the separation funnel and the mixture was distilled slowly until no more oily drops pass over.

3- the organic layer was separated, washed successively with water, 10% Na<sub>2</sub>CO<sub>3</sub>solution and then with water, dried over anhydrous calcium chloride. it is used without further purification.[6].

**Preparation of N-(4-methoxyphenyl) actamide**

- 1- (3.75gm, 0.025mol) of 4-actemido phenol were dissolved in 15mL of ethanol in a conical flask and with added potassium hydroxide solution (1.85gm, 0.033mol), in a least volume of (~ 1.5mL) by stirred magnetic stirrer.
- 2- A solution of appropriate methane bromide (0.025mol) in 12.5mL dissolved in added ethanol,
- 3- The mixture heated by using appropriate condenser for more than one hour (then 6mL distilled water added and the product was washed recrystallize for ethanol, melting point (129C°), [7].

**Preparation of 4-methoxy aniline**

- 1- In conical flask 4 N- (actamide – methoxy phenyl) (0.025mol) is dissolved in (12.5ml) ethanol and heated
- 2- Add to the mixture (3.75ml) potassium hydroxide solution (20M). the mixture was heated for three hours,
- 3- The solvent was distillation by using evaporator rotator.
- 4- The product was extract of benzene then dried by anhydrous magnesium sulfate.
- 5- The benzene was evaporated by rotary evaporator, the product has a melting point 58C° [5.6].

**Preparation of 4-alkoxy benzaldehyde**

- 1- (3.77gm) (0.025mol) of 4-hydroxy benzaldehyde dissolved in 15 mL of ethanol in a conical flask to the stirred solution and slowly was added solution of (0.033 mol) for KOH (1.85gm dissolved in less volume of water a (~ 1.5mL))
- 2- Then it was added of a solution of appropriate Alkyl bromide (0.025mol) in 12.5mL ethanol.
- 3- The mixture was heated with stirring continued stir for more than one hour. 6mL of water was added to mixture and then the product was extracted by petroleum ether and
- 4- Then washed the extract with distilled water and the solvent was evaporated, the pure product was liquid yellow color, [7].

**Preparation of Schiff bases:-**

We prepare two chain schiff bases :

**The first chain :4-(4-alkoxybenzylideneamino)benzoic acid**

- 1- equal moles number of 4- amino benzoic acid and 4-alkoxy benzaldehyde dissolved in absolute ethanol with three drops of glacial acetic acid
- 2- the mixture was heated reflux for three hours,
- 3- the mixture was cooled and washed with a small amount of ethanol and then dried the resulting
4. the compound was purified by ethanol about three once.

**The second chain 4-methoxy-N-(4-alkoxybenzylidene)aniline**

- 1- equal moles number of 4- methoxy aniline and 4-alkoxy benzaldehyde dissolved in absolute ethanol with three drops of glacial acetic acid
- 2- the mixture was heated reflux for less than hours,
- 3- the mixture was cooled and washed with a small amount of ethanol and then dried the resulting.
- 4- the compound was purified by ethanol about three once. [8]

**Results and Discussion****Identification of Prepared compound:-**

- 1-CHN analysis: all data of analysis of compounds in this table (1)

**Table (1): physical properties of compounds & Elemental analysis**

Compound Symbol	Positivism Formula	M.wt g/mol	C%		H%		N%	
			Calc	found	Calc	found	Calc	found
M4	C <sub>17</sub> H <sub>19</sub> NO <sub>2</sub>	269.34	75.81	75.885	7.11	7.113	5.20	4.227
M6	C <sub>20</sub> H <sub>25</sub> NO <sub>2</sub>	311.42	77.14	76.774	8.09	7.635	4.50	4.137
C5	C <sub>19</sub> H <sub>21</sub> NO <sub>3</sub>	311.37	73.29	72.920	6.80	6.045	4.50	4.095
C7	C <sub>21</sub> H <sub>25</sub> NO <sub>3</sub>	339.34	74.31	73.872	7.42	7.014	14.31	3.878

**2- FT.IR-spectra :** which gave good indicators about all data of functional groups in prepared compounds

1. absorption band at 1116 due to ether -O-CH<sub>2</sub>-CH<sub>2</sub>
2. absorption band at 1154 due to ether -O- CH<sub>3</sub>
3. absorption band at 1624 due to imine group CH = N
4. absorption band at 2968 due to aliphatic CH
- 5- absorption band at 3043 due to aromatic CH

1. absorption band at 1168 due to ether -O-CH<sub>2</sub>-CH<sub>2</sub>
2. absorption band at 1618 due to imine group CH = N
3. absorption band at 1207 due to ether -O- CH<sub>3</sub>
4. absorption band at 2912 due to aliphatic CH
- 5- absorption band at 3032 due to aromatic CH

**3- HNMR spectra :** all peaks appeared in figures

#### **nuclear magnetic resonance spectrum of the compound C5**

1. peaks at (0.90-1.80)ppm due to alkyl groups (CH<sub>3</sub>CH<sub>2</sub> CH<sub>2</sub> CH<sub>2</sub>)
2. peaks at (6 2.5) ppm solvent due to DMSO-d
3. peaks at ( 3:41) ppm solvent due to O-CH<sub>2</sub>
- 4.peaks at (6.62-7.84)ppm due to phenyl ring
5. peaks at (8.41))ppm due to (CH = N)
6. peaks at (13:28) ppm due to Carboxyl group

#### **HNMR spectrum of the compound C7**

1. peaks at (0.90-1.50)ppm due to alkyl groups (CH<sub>3</sub>CH<sub>2</sub> CH<sub>2</sub> CH<sub>2</sub>)
2. peaks at (2.5) ppm solvent due to DMSO-d
3. peaks at ( 3:5) ppm solvent due to O-CH<sub>2</sub>
- 4.peaks at (6.61-7.42)ppm due to phenyl ring
5. peaks at (8. 11))ppm due to (CH = N)
6. peaks at(12.98) ppm due to Carboxyl group

#### **HNMR spectrum of the compound M4**

1. peaks at (0.90-1.70)ppm due to alkyl groups (CH<sub>3</sub> CH<sub>2</sub> CH<sub>2</sub>)
2. peaks at (2.5) ppm due to solvent DMSO-d
3. peaks at ( 3:10) ppm due to O-CH<sub>3</sub>
- 4- . peaks at (3.30-3.60) ppm due to OCH<sub>2</sub>CH<sub>2</sub>
- 5.peaks at (6.97-7.47)ppm due to phenyl ring
6. peaks at (8.55))ppm due to (CH = N)

#### **HNMR spectrum of the compound M6**

1. peaks at (0.74-2.42)ppm due to alkyl groups (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-)
2. peaks at (2.5) ppm due to solvent DMSO-d
3. peaks at ( 3:43) ppm due to O-CH<sub>3</sub>
- 4- . peaks at 3.93 ppm due to OCH<sub>2</sub>CH<sub>2</sub>
- 5.peaks at (7.16-7.39)ppm due to phenyl ring
6. peaks at (8. 30))ppm due to (CH = N)

### **REFERENCES**

1. O. lehmann, "Liquid Crystal", Ber 1908; 41:3774
2. Maier W. and Saupe A.; Saupe "Eineinf achemolekular etheorie des nematis chen kristallin flussigen zustandes". Z. Naturforsch. A (in German)1958.13: 564-566
3. G.W.Gray," The Chemistry of Liquid Crystal ",Philosophical transaction of the society of London1983 ,series.A,Ch.1,p.77,
4. S.T.,L.K. ,Ong, S.T. Ong, G.Y. YeapandJ.P.W. Wong ., " Synthesis and mesomorphic properties of new Schiff base esters with different alkyl chains". Chin. Chem. Lett., 2009, 20: 767-770
5. Anthony S. Travis "Manufacture and uses of the anilines: A vast array of processes and products" In ZviR appoport., The chemistry of Anilines 2007 Part 1. Wiley. p. 764. [ISBN 978-0-470-87171-3](https://doi.org/10.1002/9780470871713)
6. A.I. Vogel , "Practical Organic Chem. Longman ", FIFTH EDITION Group Ltd ., London , 1989
7. G.W. Gray ,M. Hird ,D.L. acq and K.I.Toyne , "behavior of organic compounds in liquid crystal phase " , Mol. Cryst. Liq. Cryst., 1989; 172,165
8. Gehad G Mohamed, Mohamed Mohamed Omar ,Ahmed Mohamed Hindy , " Metal Complexes of Schiff Bases: Preparation, Characterization, and Biological Activity", Turk. J Chem, 2006; 30 , 361- 382