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Preparation of Series Schiff Bases and Studying of their Liquid Crystalline Behavior

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Abstract
Our study deals with 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 methoxyOCH3 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: Calom , Pom

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 crystalsresearch ever since in 1970 where Kelker discovered the 4-methoxylbenzylidene-
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.

Experimental:

Preparation of N- (4-hydroxyphenyl) actamide

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 wasstirred until the amine completely passes in to solution .

2- To the resulting solution 25.6mL of acetic anhydride with (three drops of H_2SO_4acidconcentration) were added and stirred and then immediately was poured in a solution of (33gm, 0.402mol) of crystallizedsodium 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_2SO_4acid 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_2SO_4 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_2CO_3solution and then with water ,dried overanhydrous 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 aconical flask and with added potassium hydroxide solution (1.85gm, 0.033mol),in a lest volume of (~ 1.5mL)by stirredmagnetic stirrer .
2-A solutionofappropriate methane bromide (0.025mol) in 12.5mLdissolved in added ethanol,
3-The mixture heated by using appropriate condenserfor more then one hour(then6mL distilled water added and the product was washed recrystallizefor ethanol,melting point (129C°), [7].

Prepare of 4-methoxy aniline
1- In conical flask4 N- (actamide – methoxy phenyl)(0.025mol) is dissolved in (12.5ml) ethanol and heated
2- Add to the mixture (3.75ml) potassiumhydroxide solution (20M) .the mixture was heated for three hours,
3- The solvent wasdistillation by using evaporator rotator.
4- The product was extractof benzene then dried byanhydrous magnesium sulfate.
5-The benzene was evaporatedbyrotary evaporator , the product has a melting point $58C^0$ [5.6].

Prepare of 4-alkyloxy banzaldehayd
1- (3.77gm)(0.025mol,) of 4-hydroxy banzaldehayd dissolved in 15 mL of ethanol in aconical flask to the stirred solution and slowlywas 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 bypetroleum ether and
4- Then washedthe extract with distillatedwater and the solvent was evaporated, the pure product was liquid yellow color , [7].

Prepare 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 acidand 4-alkyloxy banzaldehayd dissolved inabsoluteethanol with three drops of glacialacetic 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.thecompoundwas purified by ethanol about three once .
The second chain4-methoxy-N-(4-alkoxybenzylidene)aniline
1- equal moles number of 4- methoxy aniline and 4-alkyloxy banzaldehayd dissolved in absolute ethanol with three drops of glacialacetic 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]

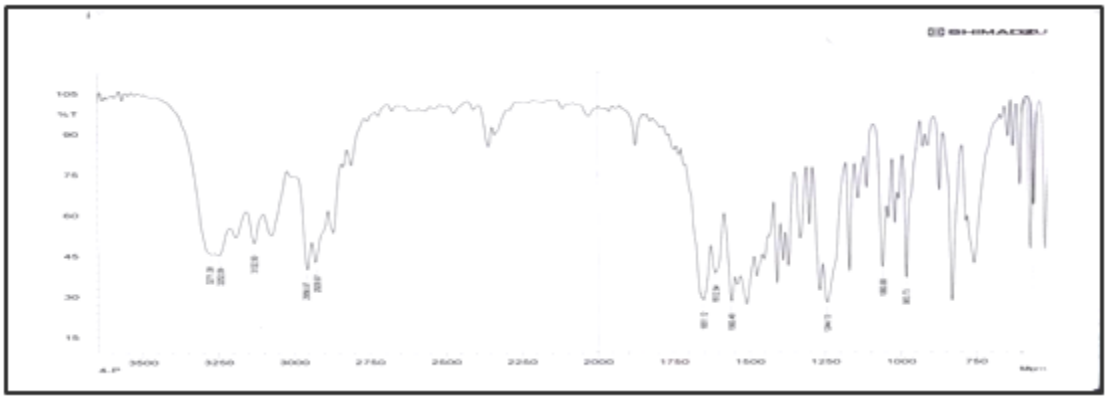


Figure (1) infrared spectrum of the compound4-mehoxy actamide

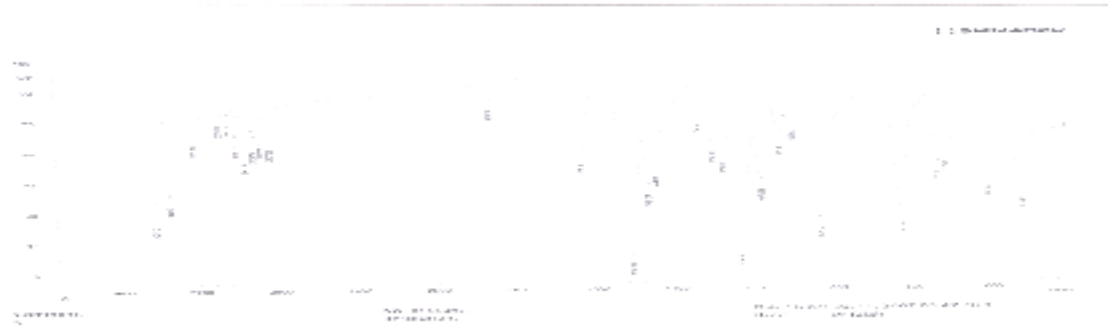


Figure (2) infrared spectrum of the compound 4-alkoxy aniline

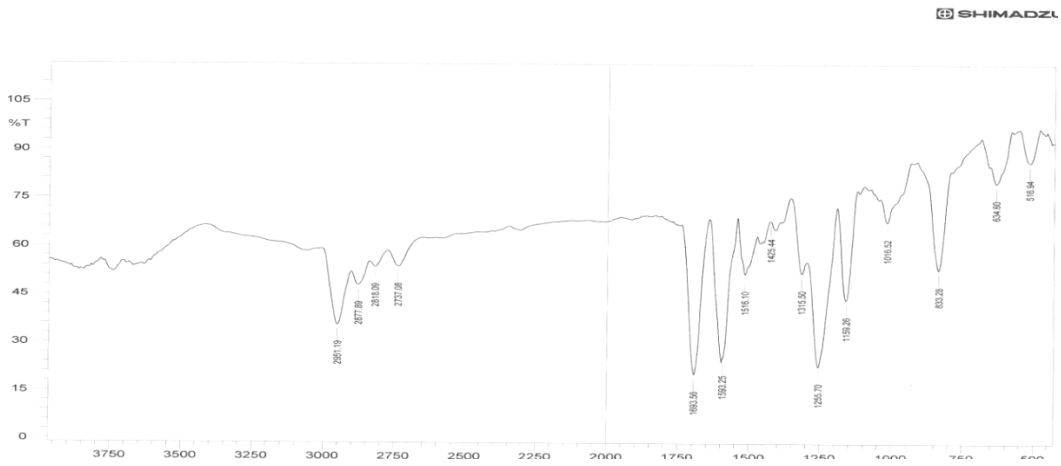
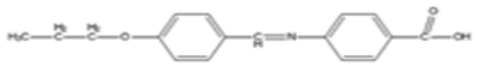
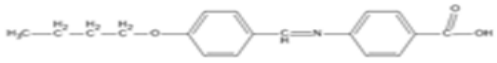
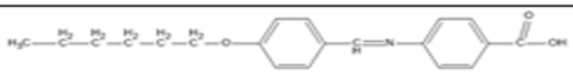
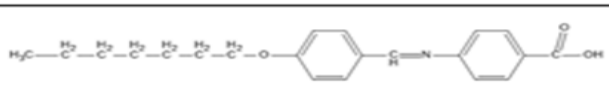
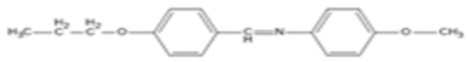
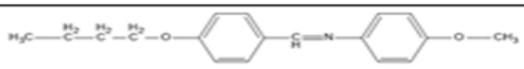
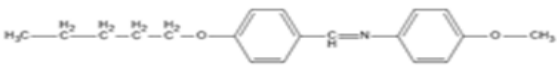
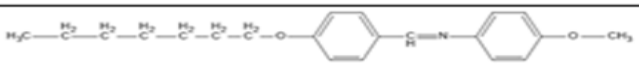


Figure (3) infrared spectrum of the compound4-alkoxy banzaldehayd

Table (1) chemical structures and melting point , color and yield of the prepared compounds

Seq.	Symbol of compound	color	m.p C⁰	Chemical structure	Product	M.w
1	C3	Yellow	194 C°		51%	283
2	C4	Yellow	183 C°		72%	297
3	C5	Yellow	158 C°		63%	311
4	C6	Yellow	169 C°		66%	325
5	C7	Yellow	158 C°		%69	339
6	M3	Silver	118 C°		85%	269
7	M4	Silver	112 C°		87%	283
8	M5	Silver	90 C°		81%	297
9	M6	Silver	104 C°		86%	311
10	M7	Silver	108 C°		79%	325

Results and Discussion

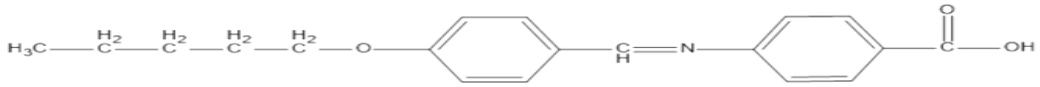
Identificationof Prepared compound:-

1-CHN analysis: all data of analysis of compounds in this table (2

Table (2): physical properties of compounds&Elemental analysis

Compound Symbol	Positivism Formula	M.wt g/mol	C%		H%		N%	
			Calc	found	Calc	found	Calc	found
M4	$C_{17}H_{19}NO_2$	269.34	75.81	75.885	7.11	7.113	5.20	4.227
M6	$C_{20}H_{25}NO_2$	311.42	77.14	76.774	8.09	7.635	4.50	4.137
C5	$C_{19}H_{21}NO_3$	311.37	73.29	72.920	6.80	6.045	4.50	4.095
C7	$C_{21}H_{25}NO_3$	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



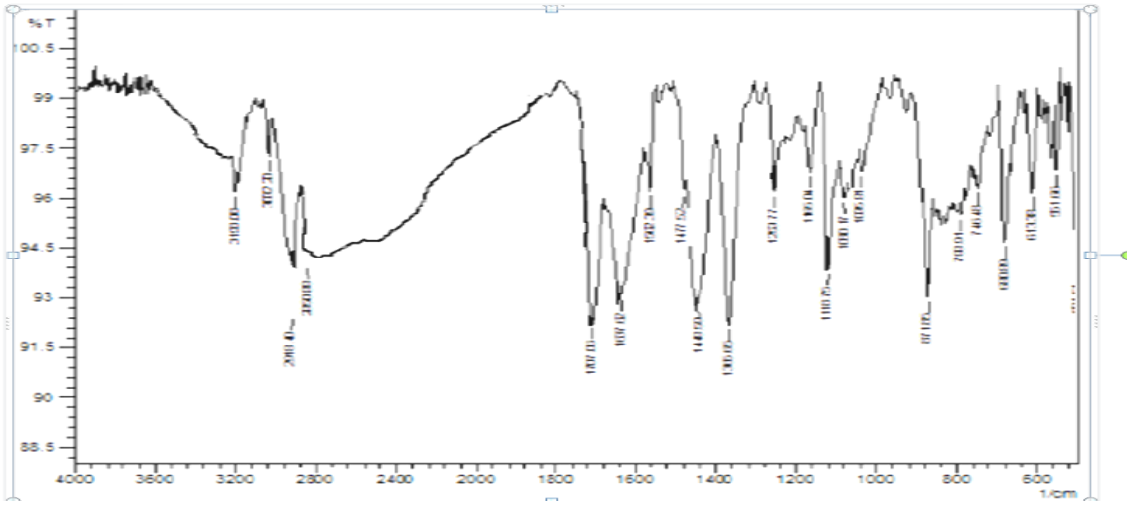
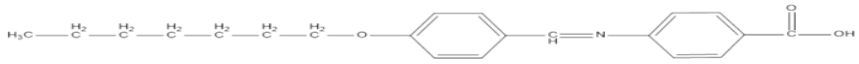


Figure (4) infrared spectrum of the compound C5

1. absorption bands at 1118 due to a group -O-CH_2-CH_2
2. absorption bands at 1618 due to imine group CH = N
3. absorption bands at 1737 due to the carbonyl group carboxylic
4. absorption bands at 2918 due to aliphatic CH
5. absorption bands at 2600-3198 due to OH of the carbonyl
6. absorption bands at 3032 due to aromatic CH



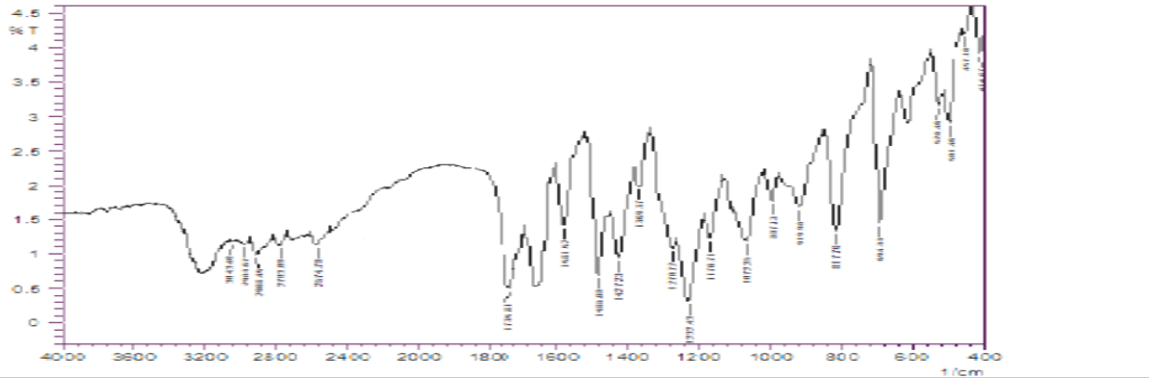


Figure (5) infrared spectrum of the compound C7

From IR spectrum of a compound most important absorption bands represent functional groups are:

1. absorption band at 1170 due to a group -O-CH_2-CH_2
2. absorption band at 1630 belonged due to imine group CH = N
3. absorption band at 1735 due to the carbonyl of carboxylic group
4. absorption band at 2983 due to aliphatic CH
5. Broadband absorption at 2574-3200 due to OH of Carbonyl group .
6. absorption band at 3034 due to aromatic CH

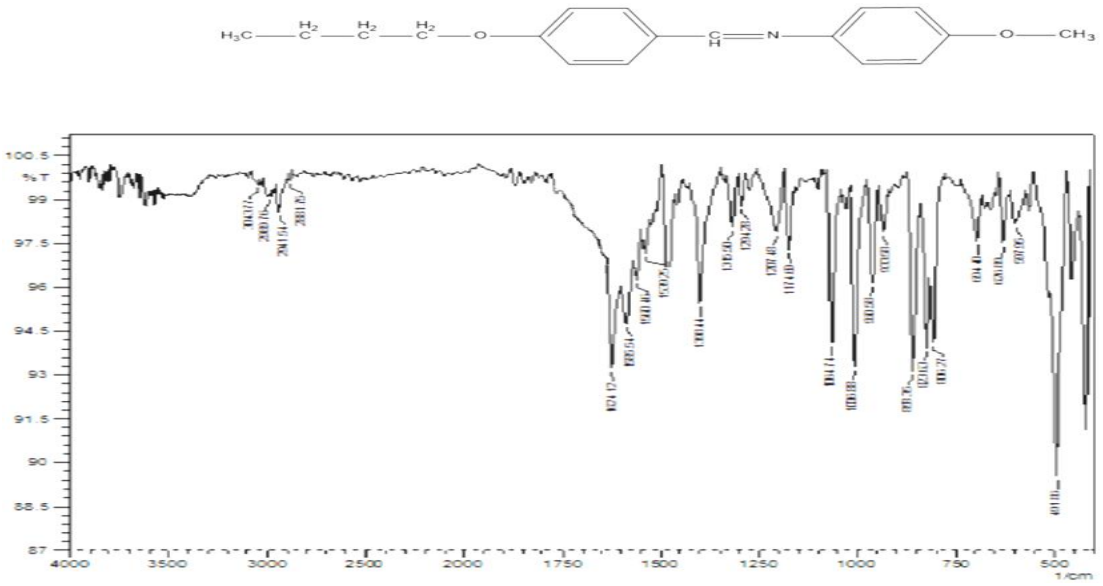


Figure (6) infrared spectrum of the compound M4

1. absorption band at 1116 due to ether -O-CH_2-CH_2
2. absorption band at 1154 due to ether -O- CH_3
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

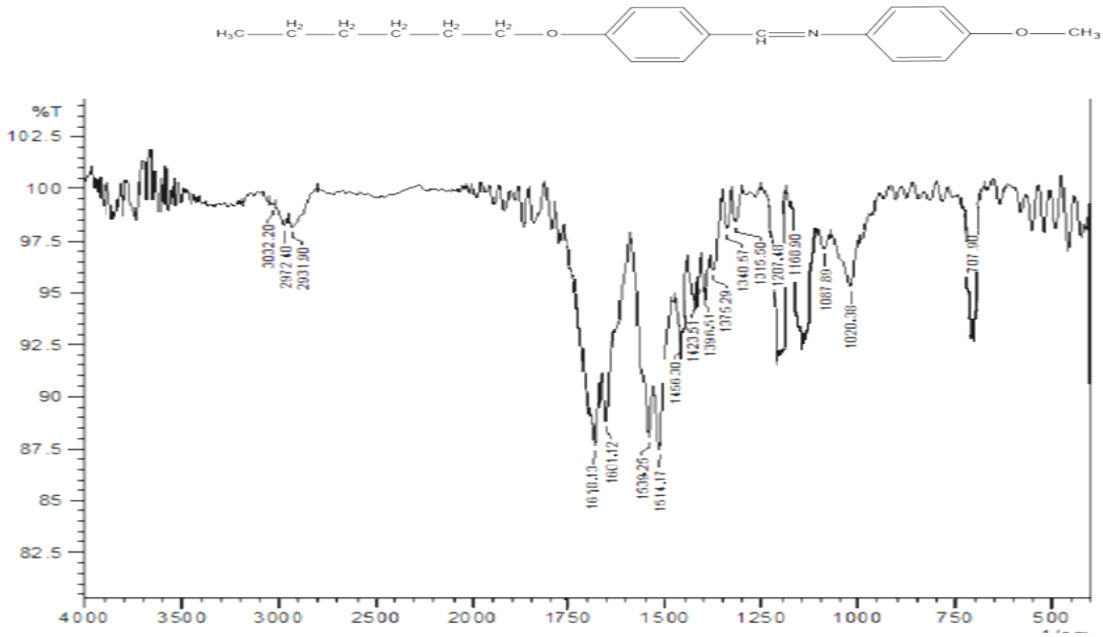


Figure (7) infrared spectrum of the compound M6

1. absorption band at 1168 due to ether -O-CH_2-CH_2
2. absorption band at 1618 due to imine group CH = N
3. absorption band at 1207 due to ether -O- CH_3
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

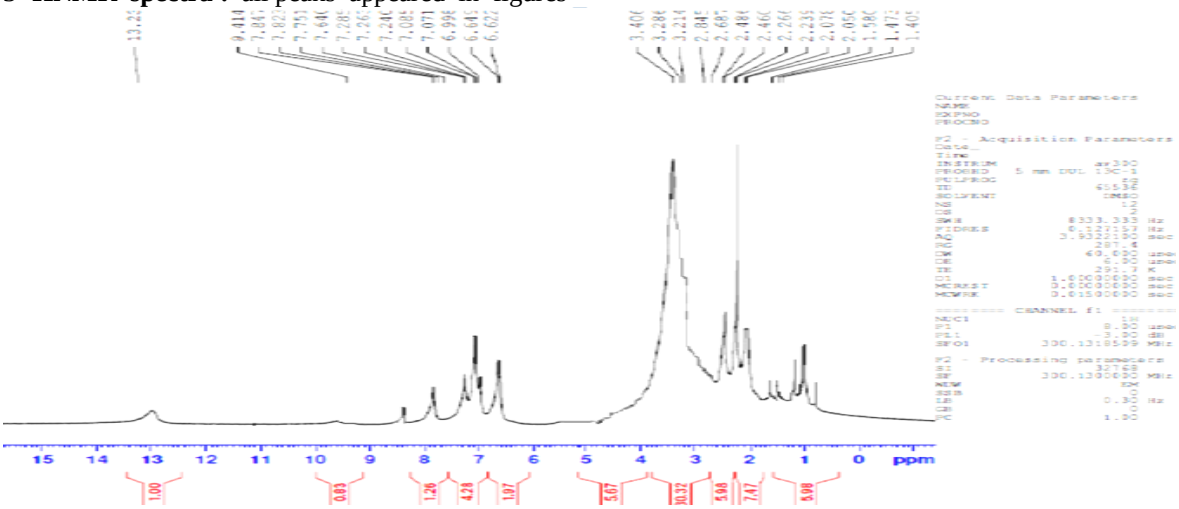


Figure (8), nuclear magnetic resonance spectrum of the compound C5

1. peaks at (0.90-1.80)ppmdue to alkyl groups (CH_3CH_2 CH_2 CH_2)
2. peaks at (6 2.5) ppmsolvent due to DMSO-d
3. peaks at (3:41) ppmsolvent due to O-CH_2
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

References

1- GehadG Mohamed, Mohamed MohamedOmar ,Ahmed Mohamed Hindy ," Metal Complexes of Schiff Bases: Preparation,Characterization, and Biological Activity", Turk. J Chem, 2006; 30 , 361- 382.

2- O.lehmann,"Liquid Crystal" ,Ber 1908;41:3774

3- Maier W. and Saupe A.; Saupe "Eineeinfachemolekularetheorie des nematischenkristallinflussigenzustandes". Z. Naturforsch. A (in German)1958.13: 564-566

4- G.W.Gray,"The Chemistry of Liquid Crystal ",Philosophical transaction of the society of London1983 ,series.A,Ch.1,p.77,

5- S.T.,L.K. ,Ong, S.T. Ong, G.Y. YeapandJ.P.W. Wong ., " Synthesis andmesomorphic properties of new Schiff base esterswith different alkyl chains". Chin. Chem. Lett., 2009, 20: 767-770

6- Anthony S. Travis "Manufacture and uses of the anilines: A vast array of processes and products" In ZviRappoport., The chemistry of Anilines 2007 Part 1. Wiley. p. 764. ISBN 978-0-470-87171-3

7- A.I. Vogel , "Practical Organic Chem. Longman "., FIFTH EDITION Group Ltd .,London , 1989

8- 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

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