SYNTHISES AND STUDY THE MESOMORPHIC PROPERTIES OF NEW TWO SERIES OF COMPOUNDS CONTAINING AZO METHINE LINKAGE

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Abstract

Two series of Schiff's bases compounds have been prepared. The new compounds having the name 4 (4$^{\backslash}$-Flouro benzoyloxy) benzylidene-*p*-substituted aniline and 4 (4$^{\backslash}$- Methoxy benzoyloxy) benzylidene–*p*-substituted aniline .The new derivatives were prepared from the reaction between different substituted aniline and 4(4$^{\backslash}$-Flouro benzoyloxy) benzaldehyde, 4(4$^{\backslash}$-Methoxybenzoyloxy) bezaldehydes (Schiff's bases) in presence of glacial acetic acid and absolute ethanol.

The resulted compounds were exhibited liquid crystalline properties .The liquid crystalline properties were studied by hot–stage polarizing microscopy and confirmed by DSC (differential Scanning Calorometry) studies.

All products show nematic mesophase.

The molecular structures of the resulted compounds were identified by IR spectra and H^1NMR for starting material, Mass spectrum also for starting material and the melting points were checked .

Introduction

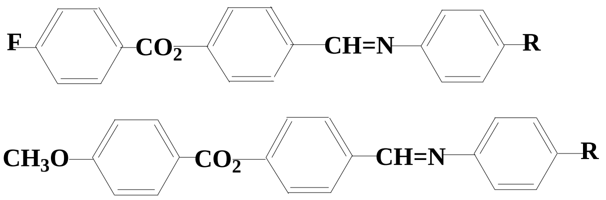
The correlation between chemical structure and mesomorphic properties is one of the most important problems in liquid crystals (LC) science .Knowledge about the influence of different structural elements of the molecules on the physico–chemical characteristics of mesomorphic organic compounds allows chemists to synthesize LC with the required properties .

Many compounds which form liquid crystals mesophases contain a para substituted benzene ring as the central group .The contribution of this ring to mesophase stability appears to lie in its rigidity ,linearity and polarizability(1-2). But, Verbit et.al.,(3) discovered that density in the central group is not a necessary condition for mesophase formation. Hence, a varity of central groups have been reported (e.g. CH=N azomethine, C=C, N=N, etc).

Thus, large number of compounds which form liquid crystal properties containing azomethine linkage or heterocyclic rings(4-7).Parra et.al.,(8,9) reported synthesis and studying the liquid crystalline properties of some organic compounds containing Schiff bases (azomethine linkage) .All these compounds showed poly mesomorphic enantiotropic nematic and smectic (Sc) phases .

Parra and his co-workers (10) also prepared a new series of liquid crystalline compounds containing azomethine linkage with thiadiazole ring.

In this paper we reported the synthesis and mesomorphic properties of new Schiff bases linkage (series 1, 2) which have the following structural formula [IX].



R $=$ **OCH_3 ,NO_2**

We compared these compounds (series 1, 2) with their analogues containing azomethime linkage (series 5), previously synthesized and reported by us (11).(see Fig.1).

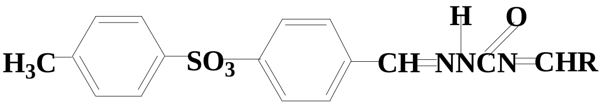


Fig. : (1)

Experimental part

Materials

All chemicals employed were of analytical reagent grade and were used without further purification .IR spectra were performed on a pye-unicam sp 1025 spectrophotometer at a rang between 625-3800 cm^{-1} as KBr film .Melting points were determined by using a calibrated mettler FBS melting apparatus. Optical observations were performed by a leitz microscope (laborlux 12 pol.) equipped with heating stage (leitz 350), and photographic camera (Vario orthmate 2).

H^{-1}NMR spectrum and mass spectrum for starting material was recorded on FT-EX 90 JEOL type NMR spectrophotometer using (CD_3OD) as a solvent and TMS as internal reference. Microanalysis of the compounds were carried out on a perkin-Elmer 240c elemental analyzer. The abbreviations (str.) and (bend.) are used to indicate stretching and bending bends, respectively.

1- Prepration of 4-Flouro benzoyl chloride$^{(12)}$.

3p-flouro benzoyl chloride was prepared by reacting 4-flouro benzoic acid with thionyl chloride with two drops of (DMF) and the mixture was heated till evolution of hydrochloric acid ceases .Excess of thionyl chloride is distilled off .(m.p.= 95^0C) yield 80% (21).

2-Preparation of 4-Flouro(Methoxy)benzoyloxy benzaldehyde

(0.1mole) of p-flouro(methoxy) benzoyl chloride in (5ml DMF)was added dropwise to the solution of 4-hydroxy benzaldehyde and (15ml)of triethyl amine in (10 ml DMF) with stirring After additional ,stirring continuous at room temperature for 24 hour .Then filtered and re-crystallized from 95 % ethanol).

With crystals m,p=109-203^0C,Yield=75% (21).

IR (KBr),υ 1730-1750 (-C=O) ,υ (2695-2830) (C-H str.),υ 1390 (C= O bend.)cm^{-1} .$^{(22)}$.

General procedure for the preparation of Schiffs bases :

4-(4$^\backslash$-flouro (methoxy) benzylidene-p-substituted aniline$^{(13)}$.

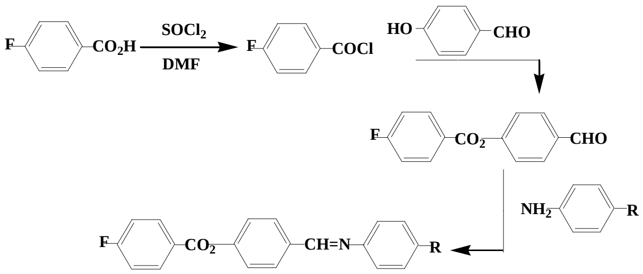
A mixture of p-flouro carboxylate bezaldehyde (0.01mole), and (0.01mole) of p-substituted aniline (0.01mole),one drop of glacial acetic acid and absolute ethanol as a solvent was refluxed for 1 hour. The solvent was removed and the resulting solid was re-crystallized from ethanol (the physical properties of the prepared compounds are listed in Table (1).

Table (1)
physical properties of the prepared compounds(series 1).

R	M.P ^{0}C	Colour	Yield	C.H.N(Calc/Found C% H% N%
H	164-166	Yellow	70%	75.24/75.09 4.3/4.25 4.39/4.32
OCH_3	265	= =	75%	72.21/72.12 4.58/4.49 4.0/3.39
I	221	= =	65%	53.93/53.79 2.9/2.8 3.1/3.07
Br	235	= =	75%	60.3/60.2 3.27/3.18 3.5/3.47
Cl	218	= =	80%	67.8/67.7 3.6/3.6 3.9/3.8
NO_2	236	= =	90%	65.93/65.85 3.5/3.5 7.69/3.62

Results and Discussion

The reaction pathway used to prepare the Schiff bases is shown in scheme (1).



R=H,-OCH_3,-I,-Br,Cl,-NO_2

Scheme (1)

The starting material was prepared from the reaction between p-flouro benzoyl chloride and p-hydroxy benzaldehyde. The starting material was characterized by IR, H^1 NMR and mass spectra.

For starting material, the reaction was followed by appearance of the following bands IR :υ3120-3160 (CH str..Ar.), 2880 cm^{-1} (C-Hstr. ald.),1744.5 cm^{-1}(C=O str.ester), 1705 cm^{-1}.$^{(14)}$ Fig.(2).

Table (2)
IR spectral data for the prepared compounds (series 1).

Comp.No.	R	υC-H arom.	υC-C=O est.	υC=N imine	υ C=C arom.	δC-H out of plane.	Others	υ (C=O) O.
IXa	H	3100	1740	1630	1600	825	–	1200
IXb	CH_3O	3095	1735	1625	1605	830	υC-H aliph.2930	1210
IXc	I	3100	1735	1630	1605	815		1295
IXd	Br	3120-3090	1735	1630	1605	885	–	1200
IXe	Cl	3135	1735	1630	1610	875	–	1200
IXf	NO_2	3100	1755	1630	1605	890	NO_2 1530-1510 broad	1200

The structures of the new derivatives were followed by disappearance of (C=O) aldehyde in the region (1690-1705) $cm^{-1}$and appearance of the band (C=N) at (1625-1630) cm^{-1} Fig.(3) for the compound IXa as an example .The physical properties of the prepared compounds are listed in Table (1) .

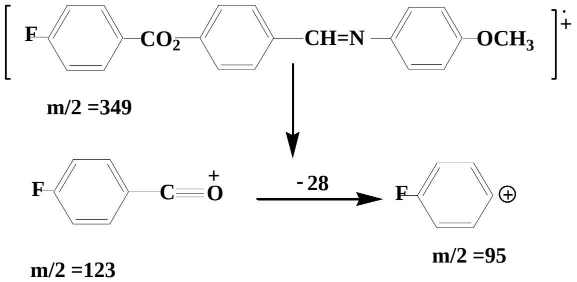
The characteristic bands of the prepared compounds are listed in Table (2).

H^1 NMR spectra are in accordance with the formula for each of compound of the series.

The H^{-1} NMR spectrum of the compound IXb is shown in Fig.(4) as example.H^1NMR (CD_3OD) as a solvent : δ (8.35-6.95) (m,12H,3C_6H_4) and azo methane H); δ(8.85) (s,3H,OCH_3) .

Mass spectrum of the compound IXb is indicating the presence of the parent ion in ratio m/e=349, according to these data, the expected molecular formula of this compound $C_{27}H_{16}NFO_3$.

The fragmentation of the compound can be illustrated by the following Scheme.



Scheme (2) : Fragmentation of compound IXb .

In this work, all the prepared compounds exhibited nematic mesophase except IXa as we see in Fig. (5) for compound IXd as example shows the thread like texture characteristic to nematic mesophase .

Probably, the mesomorphic properties of this series is due to that ,the imine linkage gives rise to a more plane structure ,allowing for stronger molecular interactions in liquid crystalline phase which explain the mesomorphism of the Schiff bases derivatives

The transition temperatures and enthalpies for this series are given in Table (3).

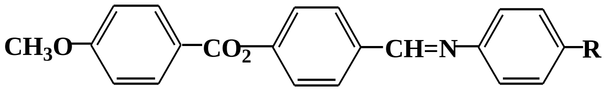
Table (3)
Transition temperatures and enthalpies for series 1.

R	T_1	T_2	Peak	ΔH kj.mol^{-1}	ΔS j.mol^{-1}.k^{-1}	Hot-stage polarizing microscopy
H	149.2	167.0	166-382	37.529	2.34×10^2	164-166 No L.C
OCH_3	249.8 150.6 141.2	272.6 164.8 151.0	259.405 154.926 148.697	0.707 27.85 2.96	0.027×10^2 1.8×10^2 0.2×10^2	K146 →N265 →I
Cl	127.4	147.4	143.376	28.505	1.99×10^2	K 124 186 195 N 221 I
Br	224.8 150.4	239.8 170.2	232.346 161.414	1.237 29.906	0.05×10^2 1.85×10^2	K 148 163 N 235 I
I	267.5 175.666	311.166 191.0	282.362 184.690	-134.27 32.07	-4.76×10^2 1.70×10^2	K 175 185 N 218 I
NO_2	198.6	172.0	162.509	30.42	1.8×10^2	K 148 N 236 I

The high $T_{N\text{-}I}$ temperature of the methoxy group, could be explained by the increasing of symmetry induced by this group to crystalline lattice stability, while more compact ,polar groups NO_2 give the highest. The low $T_{N\text{-}I}$ for compounds IXa,b,c reflects the importance of symmetry to crystalline lattice stability, because any deviation from linearity leads to diminish the liquid crystalline properties .

The absence of liquid crystalline properties of the unsubstituted compound (R=H) reflects the importance of symmetry to crystalline lattice stability, because any deviation from linearity leads to diminish the liquid crystalline properties.

Also, the second series (4,4$^{\backslash}$-Methoxy benzylidine–p-substituted aniline).

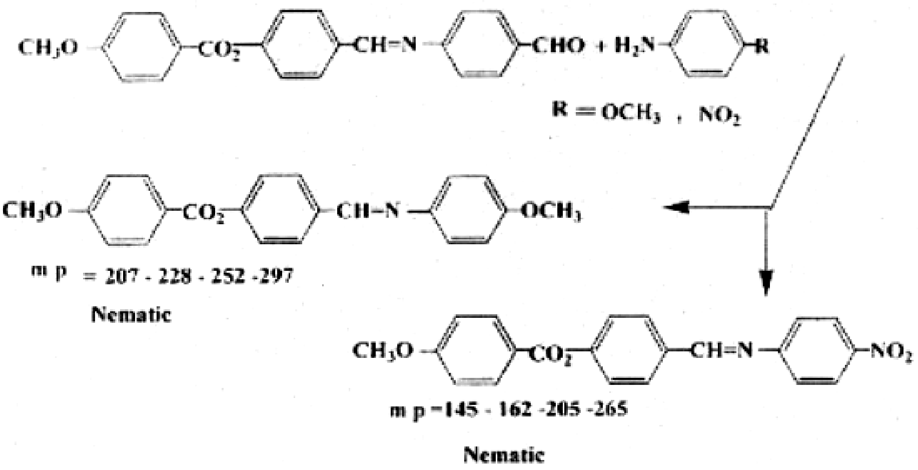


R= OCH_3 , NO_2

This series containing donating and withdrawing group in para position to azomethine linkage in order to compare the liquid crystalline properties of this series with first series.

We found that, the first one has exhibited nematic phase.

The second series has been exhibited more beautiful nematic phase and with high transition temperatures where we compared with first one, probably, this is due to withdrawing and donating group besides methoxy group in the starting material.



The size and polarity of terminal substituent seems to be the principal factors that influence the $T_{N\text{-}I}$ temperatures. Data published by Kelker, et. al., and Arora, et. al., came in parallel (15).

Dewer and Goldberg (2) pointed out that the melting point is enhanced by symmetry and strong intermolecular attractive forces; the latter are provided by polar and easily polarizable segments of the molecular.

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الخلاصة

تم في هذه الدراسة تحضير سلسلتين من قواعد شف . ان المركبات الجديدة تحمل الاسم 4-(4- فلوروبنزوايلوكسي) بنزايلدين –بارا انيلين معوض و4- (4-ميثوكسي بنزوايلوكسي) بنزايلدين –بارا انلين معوض . وقد تم تحضير المشتقات الجديدة من التفاعل بين المعوضات المختلفة للانلين و 4 (4-فلورو بنزوايلوكسي) بنزالديهايد و 4 (4-ميثوكسي بنزوايلوكسي) بنزالديهايد (قواعد شف) بوجود حامض الخليك الثلجي والايثانول المطلق. تمت دراسة الخواص البلورية السائلة بواسطة المكرسكوب المستقطب المزود بمنصة التسخين ومسعر المسح التفاضلي. وقد اظهرت جميع ا لمركبات المحضرة اطوار نيماتية (خيطية) . تم تشخيص التراكيب الكيميائية للمركبات الناتجة من خلال اطياف ال IR وHNMR و طيف الكتلة Mass spectrum للمادة الاساسية كذلك تم قياس درجات الانصهار .