Synthesis of some new Heterocyclic Compounds and Schiff bases of 4-phenyl-3-ene-butanone and study their liquid crystal properties

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Abstract

A new heterocyclic compounds(II-V)were synthesized through a reaction of compound(I) with urea,thiourea,hydrazine hydrate, and hydroxylamine hydrochloride and series of Schiff bases(VIa-d) and (VIIa-d) were synthesized from(II) and (III).The prepared compounds were characterized by (FT-IR) spectrum. Physical properties of the prepared compounds were recorded and their mesomorphic phases were investigated.

Keywords: Liquid crystal properties.

Introduction

α,β-Unsaturated ketones like Chalcons undergo a variety of useful reactions to produce a large number of their derivatives specialy heterocyclic derivatives[1-5]. A large number of Schiff bases were prepared and their biological activity were investigated and found to be very good antibacterial, antifungal agents [6-8]. Also they performed so many deferent mesophases[9,10]. Heterocyclic compounds are exhibiting a variety of mesophases[11-15].

Many Liquid crystalline substances which have exclusively smectic mesophase(structure) or exclusively nematic mesophase (structure). But some can exist as bothtypes of mesophase, smectic followed by nematic and they have definite transition temperature defining the stability of the different phase, which are always reproducible .There are substances possessing more than one smectic phase having sharp temperature range of stability of different phases. This phenomenon is known as polymorphism.

Smectic phase (Liquid Crystal) retain a two dimensional order. In the smectic phase the layer of the molecules are quite flexible. A number of different type of smectic liquid crystals are

known which differ from each other in the way of layer formation. The increased order
means that the smectic state is more "solid-like" than the nematic. Smectic – A, B, C, D,
E, F, G, H, I. A number of different classes of smectics have been recognized [16].
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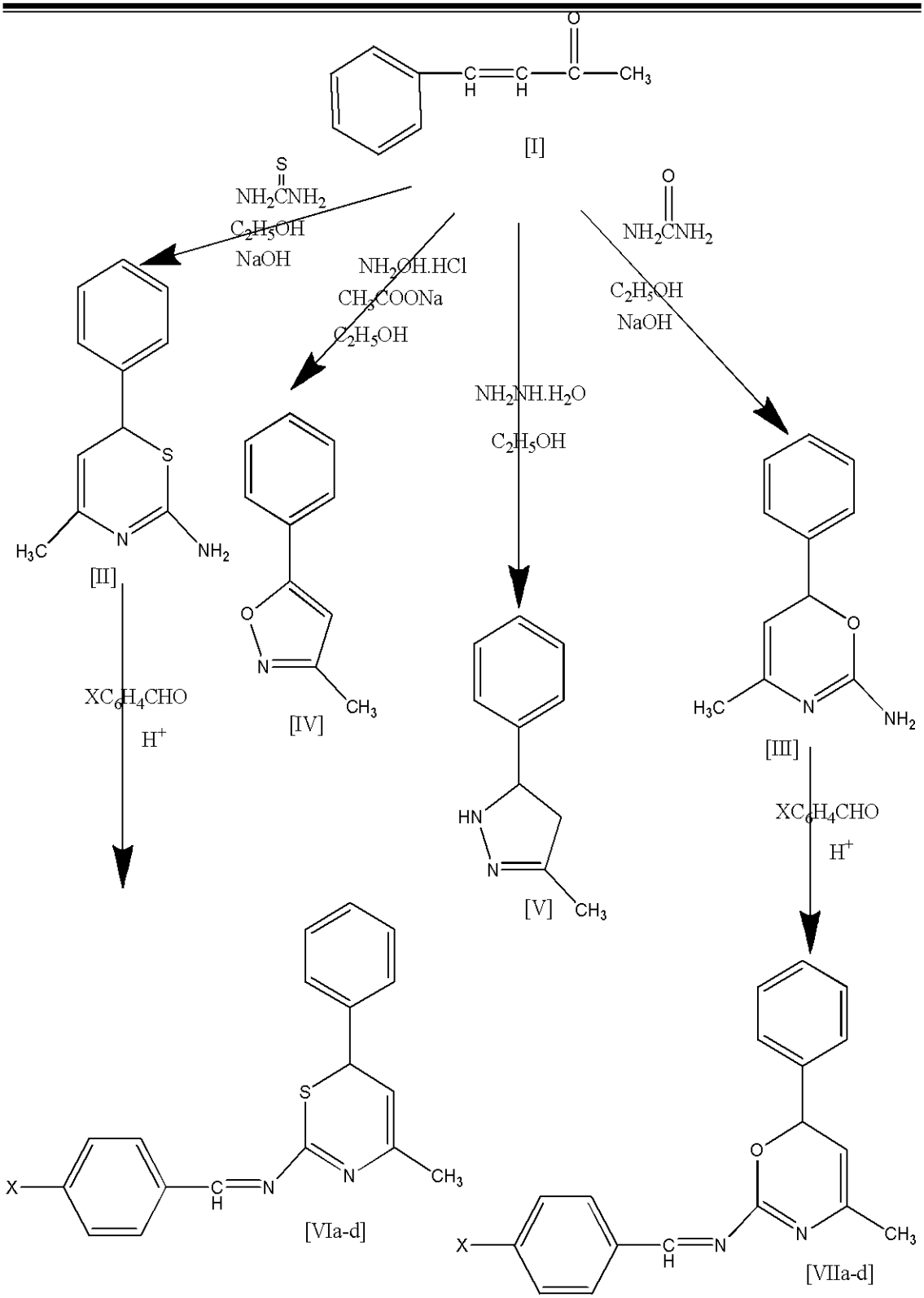
Mesomorphic behavior was observed for symmetrical and unsymmetrical azomethines, obtained from the benzene-1,4-dicarboxaldehyde and symmetrical ones prepared from 2,5-thiophene dicarboxaldehyde and different amines having aliphatic chains. mesophases were detected: nematic, smectic A, smectic C, smectic F (I), smectic G (J).[17] New liquid crystals based on calix[4]areneSchiff base were prepared by the reaction of tetraaminocalix[4] arene with
aldehydes (4-hydroxy benzaldehyde, 2-vanillin, 4-vanillin and 2-hydroxy naphthaldehyde) [18].

In the view of the above studies a series of new Schiff bases with heterocyclic units were prepared (VIa-d)&(VI Ia-d) and their mesogenic properties were investigated.



Schem-1- (where X=NO_2=a ,$N(CH_3)_2$=b ,CH_3=c ,and H=d.)

Experimental

The chemicals used in this work were purchased from their manufacturers (Fluke Co. & Merck Co.) without any more purifications ,the melting points of the prepared compounds were recorded using Stuart Scientific Melting Point (SMP_1) Apparatus without corrections. FT-IR spectrum were carried out using Shimadzu 8300-FTIR Spectrophotometer . The mesomorphic properties were investigated using polarized optical microscope type Olympus BX51M equipped with automatic photomicrographic system model PMIOSP .Hot stage was used type THM 600 .TMS 94 made by Linkam Scientific Instruments LTd.(UK).

Preparation of compounds (II) and (III)

A mixture of compound(I) (0.02mol), thiourea /urea (0.02 mol) were dissolved in ethanolic
sodium hydroxide (10ml) was stirred about 2-3 hours with a magnetic stirrer. This was then
poured into400 ml of cold water with continuous stirring for an hour and then kept in refrigerator
for 24 hours. The precipitate obtained was filtered, washed and recrystallized. Physical properties
and yield of compounds (II)and (III) are listed in table-1-

Preparation of compounds (IV)and(V)

A mixture of compound(I) (0.02 mol), hydroxylamine hydrochloride/ hydrazine hydrate
(0.02 mol) and sodium acetate in ethanol (25 ml) was refluxed for 6hr. The mixture was concentrated by distilling out the solvent under reduced pressure and poured into ice water.
The precipitate obtained was filtered, washed and recrystallized. Physical properties and yield of compounds (IV)and (V) are listed in table-1-

Preparation of Schiff bases (VIa-d)

Compound(II) (0.20mole)and the substituted aromatic aldehydes (0.20mole) were dissolved in ethanol absolute and few drops of glyciel acetic acid was added to the mixture which was refluxed for 60 min. The reaction mixture was then cooled and the prcipitate was filtred off and collected .The physical properties and the yield of the prepared compounds are listed in table -1-

Preparation of Schiff bases (VIIa-d)

The same procedure used to prepare compounds (VIa-d) using compound(III) instead of compound (II)and the physical properties and the yield of the prepared compounds are listed in table -1-.

Result and Discussion

All the prepared compounds were identified using FT-IR spectra and the data are listed in table -2,compound II showed stretching vibration at2360 cm^{-1} for (C-S-C)group , a band for (1^0NH2),at 1624 cm^{-1},and for(Ar-C=C) at1448 cm^{-1} ;while compound III showed stretching vibration at 3032cm^{-1} for(Ar CH,st),1442cm^{-1} for(Ar C=C),1334cm^{-1} for (C-N,),and a band at 1207 for (C-O-C st); while compound IV showed stretching vibration at 3394 $cm^{-1}$for (2^0NH,st) ,3062 cm^{-1} for (Ar-CH) ,14541442cm^{-1} for(Ar C=C), and aband at 1276 for (C-N);while compound V showed stretching vibration at1276 for (C-N) ,aband for (ArC-H),at3062 cm^{-1} for(Ar-C=C),1454 $cm^{-1}$for and for (2^0NH,st) ,3394 cm^{-1});while compound V Ia showed stretching vibration at 2360 $cm^{-1}$for (C-S-C,st) ,1539 cm^{-1} for(Ar-NO_2) ,1651 $cm^{-1}$for(C=N),and aband at 1103 cm^{-1} for (C-N) ;while compound V Ib showed stretching vibration at 2360 $cm^{-1}$for(C-S-C),1643 $cm^{-1}$for(C=N),and aband at1114 cm^{-1} for (C-N) while; compound V Ic showed stretching vibration at2310 cm^{-1} for(C-S-C) ,1643 $cm^{-1}$for(C=N),and aband at1114 cm^{-1} for (C-N) ; while compound V Id showed stretching vibration at 2360 cm^{-1} for(C-S-C) ,1683$cm^{-1}$for(C=N), and aband at1184 cm^{-1} for (C-N).

While compound VI Ia showed stretching vibration at 1668 cm^{-1} for(C=N) ,1539$cm^{-1}$for(Ar-NO_2),for (C-N),1192 $cm^{-1}$and aband at157 cm^{-1} for (C-O-C);while compound V IIb showed stretching vibration at 1670 $cm^{-1}$for(C=N),1186 $cm^{-1}$for(C-N),and aband at1162cm^{-1} for (C-O-C);while compound V IIc showed stretching vibration at 1651$cm^{-1}$for(C=N),1196 $cm^{-1}$for(C-N),and aband at1157cm^{-1} for (C-O-C));while compound V IIc showed stretching vibration at 1653 $cm^{-1}$for(C=N),1454$cm^{-1}$for(Ar-C=C),and aband at1157cm^{-1} for (C-O-C).

The above data confirmed the suggested chemical structure of the prepared compounds.

Table-1-Physical properties and the yield of the prepared compounds

Compounds	X		Yield(%)	Colour	M.P ^{0}C
II	------	$C_{10}H_{12}N_2S$	59	Yellow	135
III	------	$C_{10}H_{12}ON$	70	Yellow	80
IV	------	$C_{10}H_9ON$	85	White	104
V	------	$C_{10}H_{10}ON$	65	Brown	76
VIa	$-NO_2$	$C_{18}H_{15}O_2N_3S$	85	Brown	135
VIb	$-N(CH_3)_2$	$C_{20}H_{21}N_3S$	63	Brown	81
VIc	$-CH_3$	$C_{19}H_{18}N_2S$	60	==	117
VId	-H	$C_{18}H_{16}N_2S$	67	==	140
VIIa	$-NO_2$	$C_{20}H_{21}N_3O$	80	Brown	140
VIIb	$-N(CH_3)_2$	$C_{18}H_{15}O_3N_3$	75	Yellow	110
VIIc	$-CH_3$	$C_{19}H_{18}ON_2$	65	Brown	115
VIId	-H	$C_{18}H_{16}ON_2$	87	Brown	135

Table-2-FT-IR spectral data of the prepared compounds

Compounds	Formula	FT-IR (KBr)ν(cm^{-1})
II	$C_{10}H_{12}N_2S$	1624(1^0NH_2), 2360(C-S-C, st.), 1448 (Ar-C=C)
III	$C_{10}H_{12}ON$	3032(Ar CH,st),1442(Ar C=C), 1334 (C-N,st)1207(C-O-C st)
IV	$C_{10}H_9ON$	3062(Ar C-H), 1454(Ar C=C), 1662(C=N), 1172(C-O-C)
V	$C_{10}H_{10}ON$	3394(2^0NH,st) 3062(Ar C-H), 1454(Ar-C=C) 1276(C-N)
VIa	$C_{18}H_{15}O_2N_3S$	2360(C-S-C,st)1539(Ar-NO_2) 1651(C=N),1103(C-N)
VIb	$C_{20}H_{21}N_3S$	2360(C-S-C),1643(C=N),1114(C-N)
VIc	$C_{19}H_{18}N_2S$	2310(C-S-C)1643(C=N)1114(C-N)
VId	$C_{18}H_{16}N_2S$	2360(C-S-C)1683(C=N)1184(C-N)
VIIa	$C_{20}H_{21}N_3O$	1668(C=N), 1539(Ar-NO_2),1192(C-N), 1157(C-O-C).
VIIb	$C_{18}H_{15}O_3N_3$	1670(C=N),1186(C-N),1162(C-O-C)
VIIc	$C_{19}H_{18}ON_2$	1651(C=N), 1196(C-N), 1157(C-O-C).
VIId	$C_{18}H_{16}ON_2$	1653(C=N),1454(Ar-C=C),1157(C-O-C)

The prepared compounds were examined for their mesogenic properties and the results were listed in table -3.Compounds II-V did not exhibit any mesophase ,due to their molecular structures ,while compounds VIa-VId and compounds VIIa-VIId exhibited smectic A mesophase (fig-9. Show a smectic Amesophase of compound VIIb a sample of other compounds) at deferent temperatures ,since these compounds have molecular structures containing polar groups such as (C=N) group with aromatic and heterocyclic systems ,although the presence of deferent terminal groups affected the type of mesophase of the investigated compounds.

Table-3-liquid crystal properties of the prepared compounds

Compounds	Temperature ^{0}C	Mesophase
II	135	non
III	110	non
IV	106	non
V	80	non
VIa	50 135	S_A isotropic
VIb	96 117	S_A isotropic
VIc	40 63	S_A isotropic
VId	110 140	S_A isotropic
VIIa	55 110	S_A isotropic
VIIb	110 140	S_A isotropic
VIIc	45 115	S_A isotropic
VIId	107 135	S_A isotropic

S_A=smectic mesophas

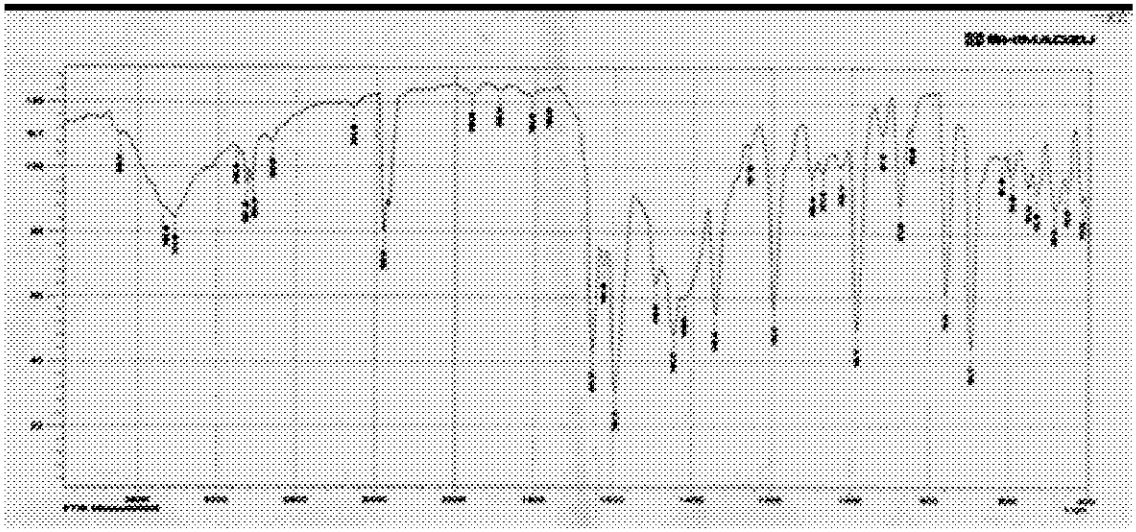


Fig. 1.FT-IR Spectrum of compound (II)

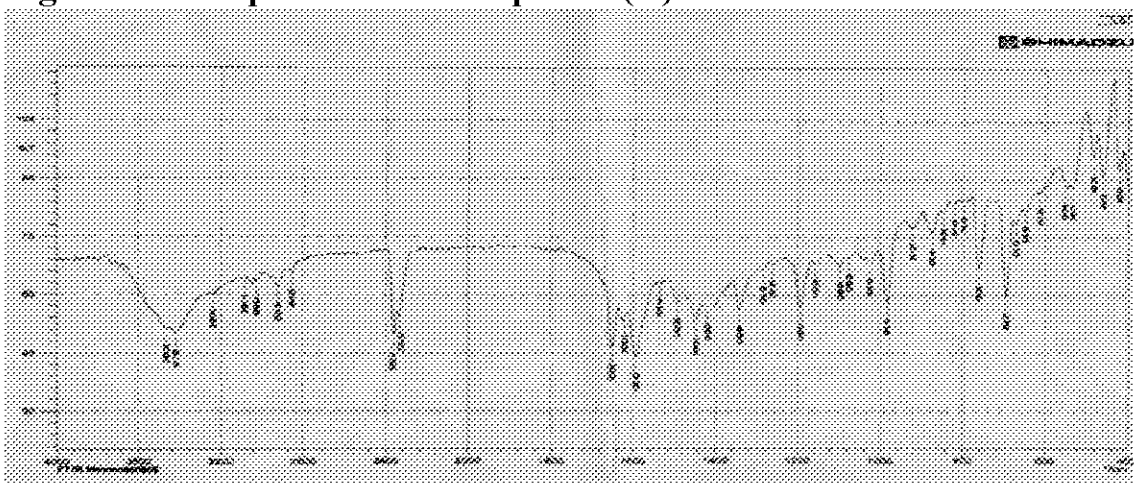


Fig. 2.FT-IR Spectrum of compound (III)

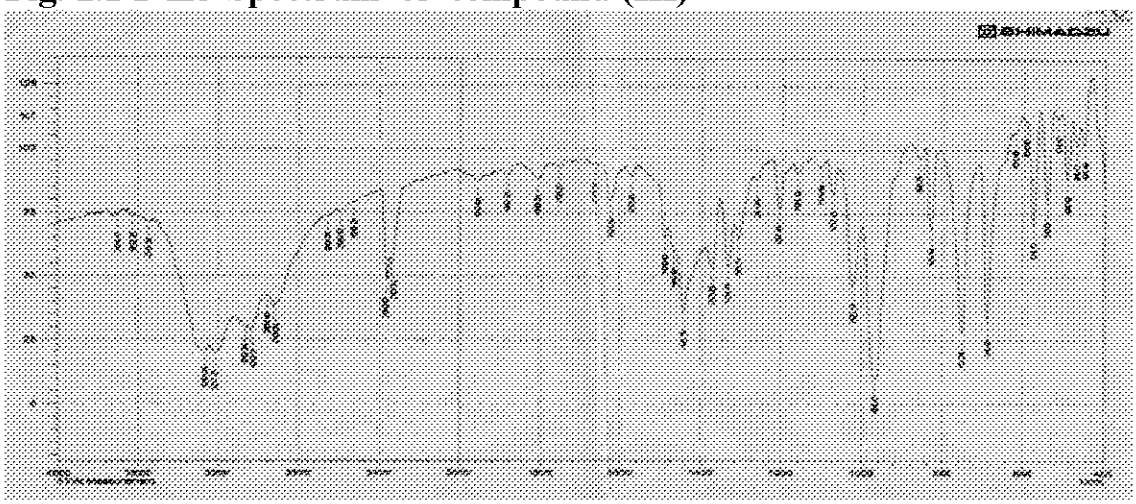


Fig. 3.FT-IR Spectrum of compound (IV)

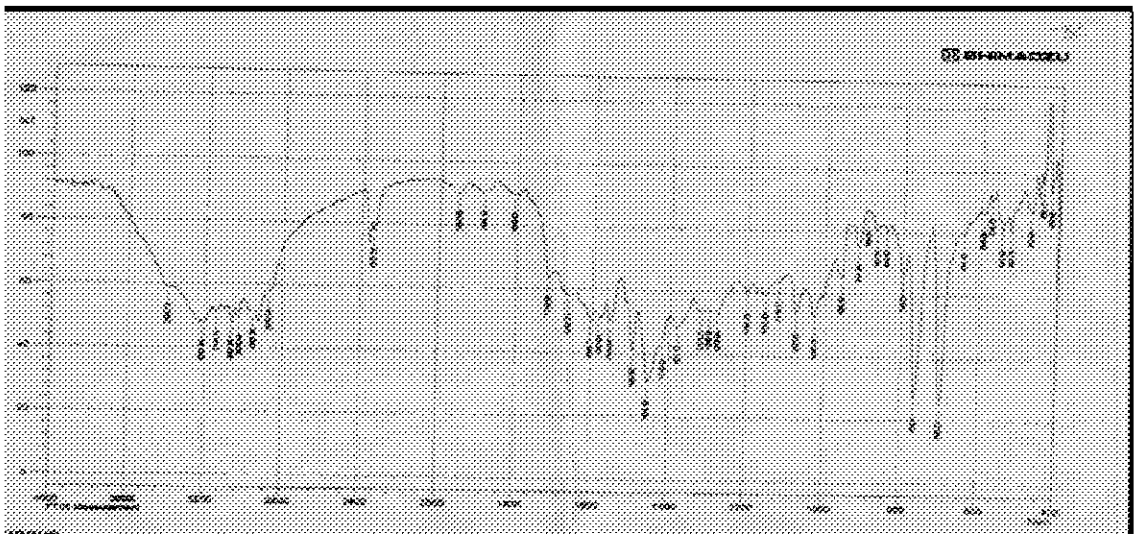


Fig. 4.FT-IR Spectrum of compound (V)

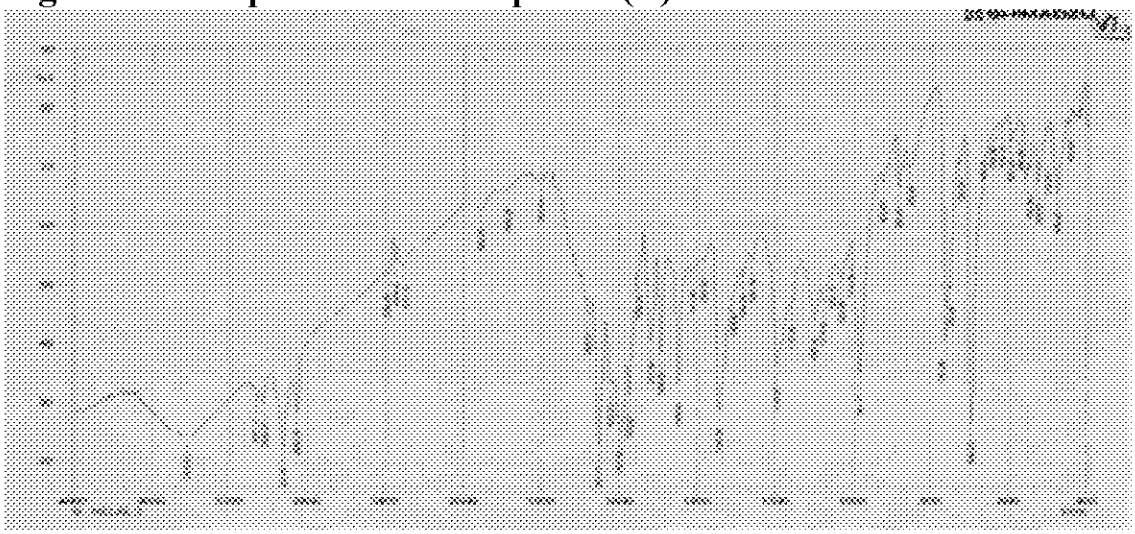


Fig.5.FT-IR Spectrum of compound (VIa)

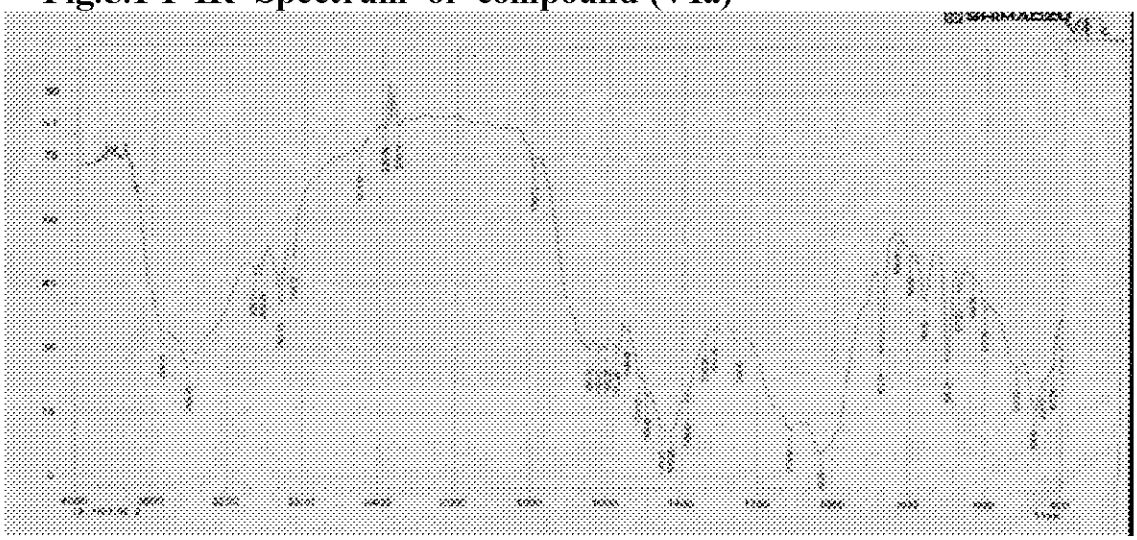


Fig. 6.FT-IR Spectrum of compound (VIb)

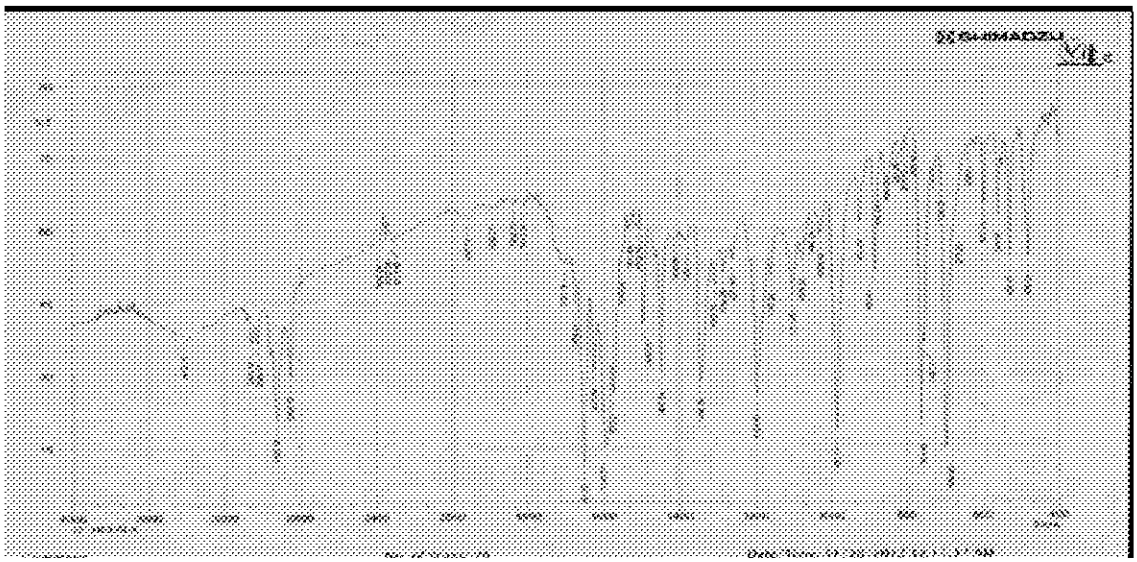


Fig. 7.FT-IR Spectrum of compound (VIc)

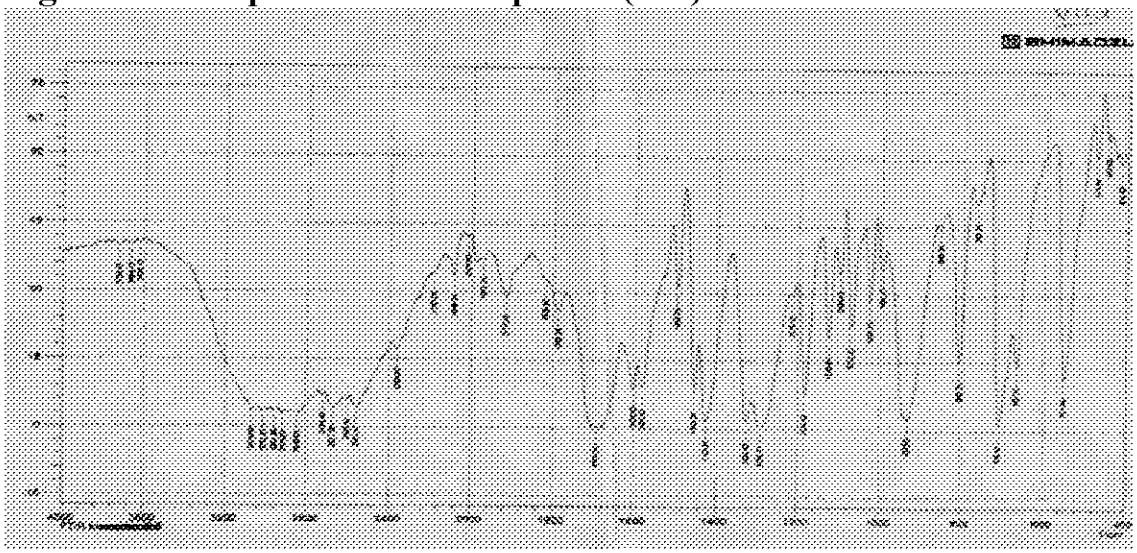


Fig. 8.FT-IR Spectrum of compound (VId)

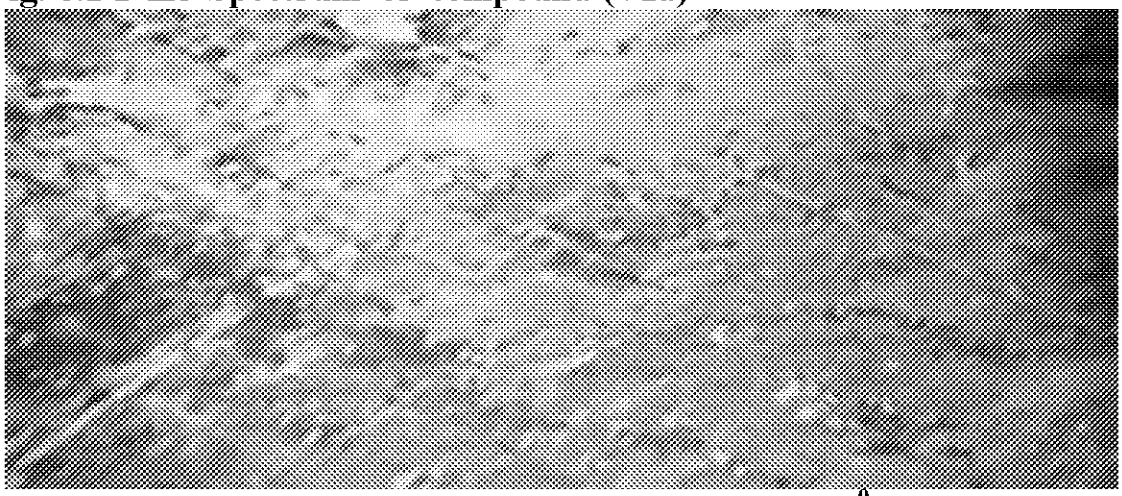


Fig-9-Smectic A texture of compound –VIIb at 120^0 C

Conclusion

We can concluate from the results obtained that the prepared compounds performing a mesophase type only smectic A due to their chemical structure, which have molecular orintation seems like solid phase.

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