

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

Hanaa G. Attiya

Chem.Dept./ College of Education Ibn-Al-Haithem

University of Baghdad.

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 Chalcones undergo a variety of useful reactions to produce a large number of their derivatives specially 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].

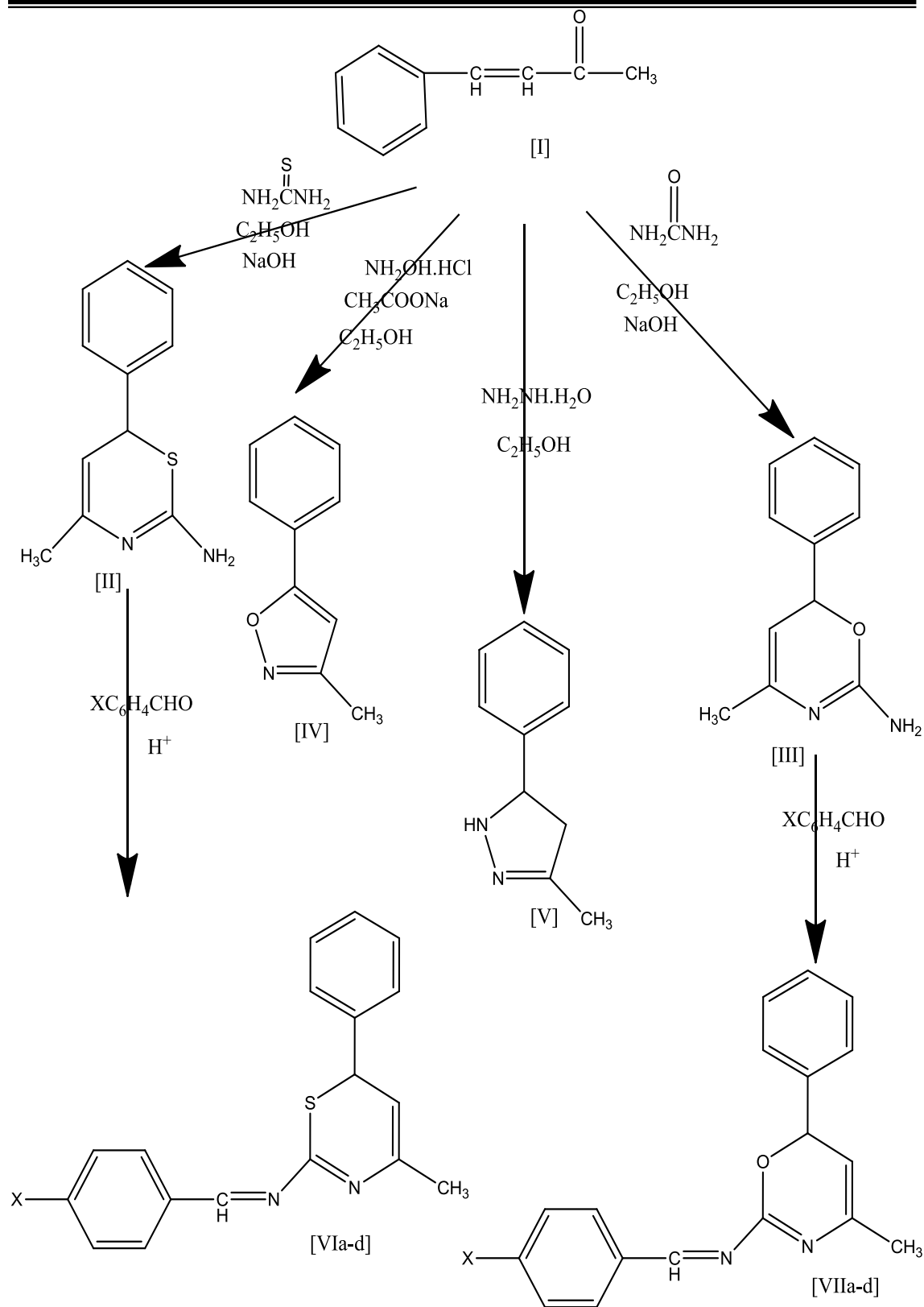
Many Liquid crystalline substances which have exclusively smectic mesophase(structure) or exclusively nematic mesophase (structure). But some can exist as bothtypes of mesophase, smectic followed by nematic and they have definite transition temperature defining the stability of the different phase, which 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].

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.

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



Schem-1- (where $\text{X}=\text{NO}_2=\text{a}$, $\text{N}(\text{CH}_3)_2=\text{b}$, $\text{CH}_3=\text{c}$, and $\text{H}=\text{d}$.)

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 (SMP₁) 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 into 400 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 precipitate was filtered 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 at 2360 cm^{-1} for (C-S-C) group, a band for (1°NH_2) , at 1624 cm^{-1} , and for (Ar-C=C) at 1448 cm^{-1} ; while compound III showed stretching vibration at 3032 cm^{-1} for (Ar CH, st), 1442 cm^{-1} for (Ar C=C), 1334 cm^{-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°NH, st) , 3062 cm^{-1} for (Ar-CH), 1454 and 1442 cm^{-1} for (Ar C=C), and a band at 1276 for (C-N); while compound V showed stretching vibration at 1276 for (C-N), a band for (ArC-H), at 3062 cm^{-1} for (Ar-C=C), 1454 cm^{-1} for and for (2°NH, 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-NO₂), 1651 cm^{-1} for (C=N), and a band 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 a band at 1114 cm^{-1} for (C-N) while; compound V Ic showed stretching vibration at 2310 cm^{-1} for (C-S-C), 1643 cm^{-1} for (C=N), and a band at 1114 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 a band at 1184 cm^{-1} for (C-N).

While compound VI Ia showed stretching vibration at 1668 cm^{-1} for (C=N), 1539 cm^{-1} for (Ar-NO₂), for (C-N), 1192 cm^{-1} and a band at 157 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 a band at 1162 cm^{-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 a band at 1157 cm^{-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 a band at 1157 cm^{-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 °C
II	-----	C ₁₀ H ₁₂ N ₂ S	59	Yellow	135
III	-----	C ₁₀ H ₁₂ ON	70	Yellow	80
IV	-----	C ₁₀ H ₉ ON	85	White	104
V	-----	C ₁₀ H ₁₀ ON	65	Brown	76
VIa	-NO ₂	C ₁₈ H ₁₅ O ₂ N ₃ S	85	Brown	135
VIb	-N(CH ₃) ₂	C ₂₀ H ₂₁ N ₃ S	63	Brown	81
VIc	-CH ₃	C ₁₉ H ₁₈ N ₂ S	60	==	117
VIId	-H	C ₁₈ H ₁₆ N ₂ S	67	==	140
VIIa	-NO ₂	C ₂₀ H ₂₁ N ₃ O	80	Brown	140
VIIb	-N(CH ₃) ₂	C ₁₈ H ₁₅ O ₃ N ₃	75	Yellow	110
VIIc	-CH ₃	C ₁₉ H ₁₈ ON ₂	65	Brown	115
VIIId	-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)v(cm ⁻¹)
II	C ₁₀ H ₁₂ N ₂ S	1624(1 ⁰ NH 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 ₉ ON	3062(Ar C-H), 1454(Ar C=C), 1662(C=N), 1172(C-O-C)
V	C ₁₀ H ₁₀ ON	3394(2 ⁰ NH, st) 3062(Ar C-H), 1454(Ar-C=C) 1276(C-N)
VIa	C ₁₈ H ₁₅ O ₂ N ₃ S	2360(C-S-C, st) 1539(Ar-NO ₂) 1651(C=N), 1103(C-N)
VIb	C ₂₀ H ₂₁ N ₃ S	2360(C-S-C), 1643(C=N), 1114(C-N)
VIc	C ₁₉ H ₁₈ N ₂ S	2310(C-S-C) 1643(C=N) 1114(C-N)
VIId	C ₁₈ H ₁₆ N ₂ S	2360(C-S-C) 1683(C=N) 1184(C-N)
VIIa	C ₂₀ H ₂₁ N ₃ O	1668(C=N), 1539(Ar-NO ₂), 1192(C-N), 1157(C-O-C).
VIIb	C ₁₈ H ₁₅ O ₃ N 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).
VIIId	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-VIId and compounds VIIa-VIIId exhibited smectic A mesophase (fig-9. Show a smectic A mesophase of compound VIIb a sample of other compounds) at different temperatures, since these compounds have molecular structures containing polar groups such as (C=N) group with aromatic and heterocyclic systems, although the presence of different terminal groups affected the type of mesophase of the investigated compounds.

Table-3-liquid crystal properties of the prepared compounds

Compounds	Temperature °C	Mesophase
II	135	non
III	110	non
IV	106	non
V	80	non
VIa	50	S _A
	135	isotropic
VIb	96	S _A
	117	isotropic
VIc	40	S _A
	63	isotropic
VIId	110	S _A
	140	isotropic
VIIa	55	S _A
	110	isotropic
VIIb	110	S _A
	140	isotropic
VIIc	45	S _A
	115	isotropic
VIIId	107	S _A
	135	isotropic

S_A=smectic mesophase

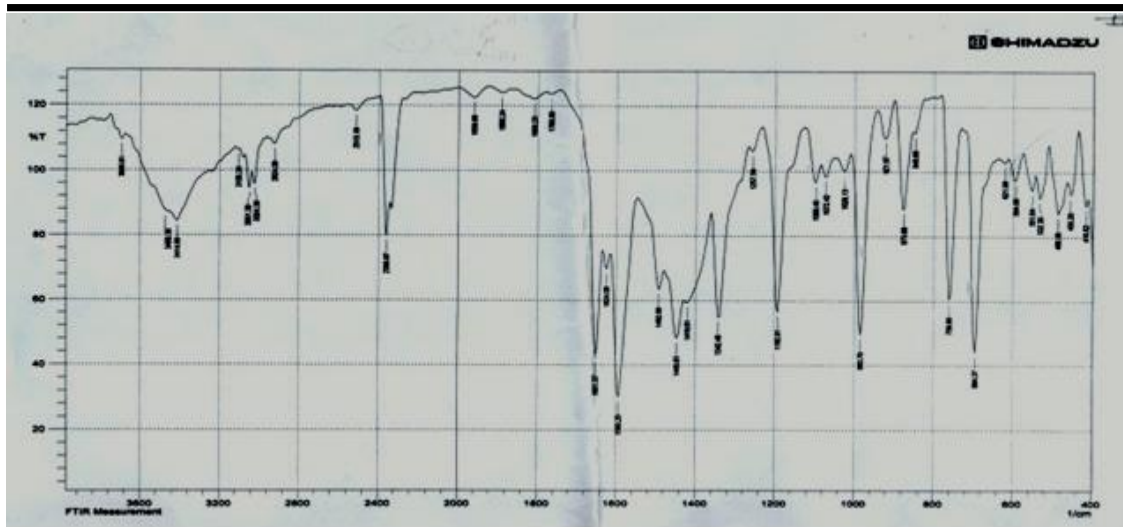


Fig. 1. FT-IR Spectrum of compound (II)

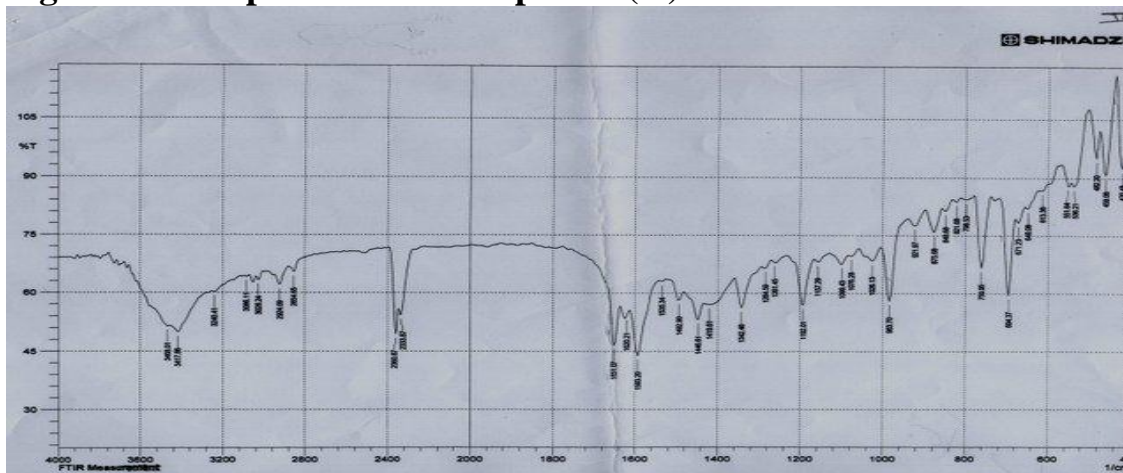


Fig. 2. FT-IR Spectrum of compound (III)

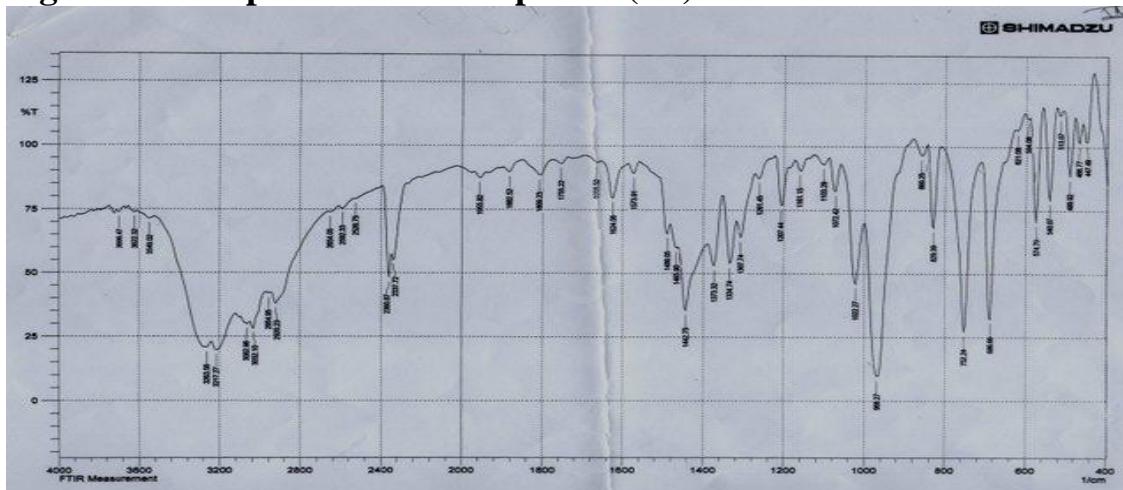


Fig. 3. FT-IR Spectrum of compound (IV)

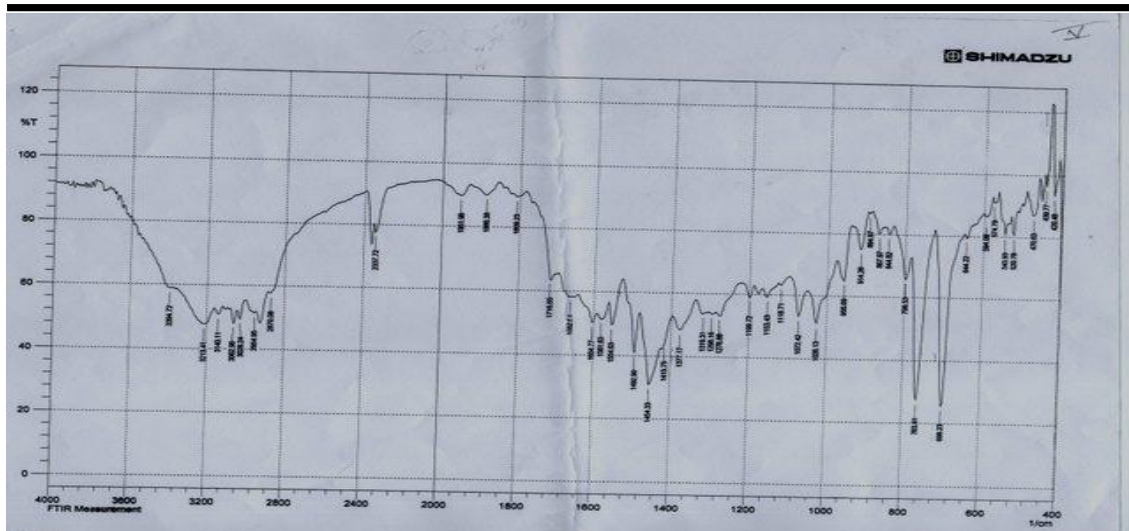


Fig. 4. FT-IR Spectrum of compound (V)

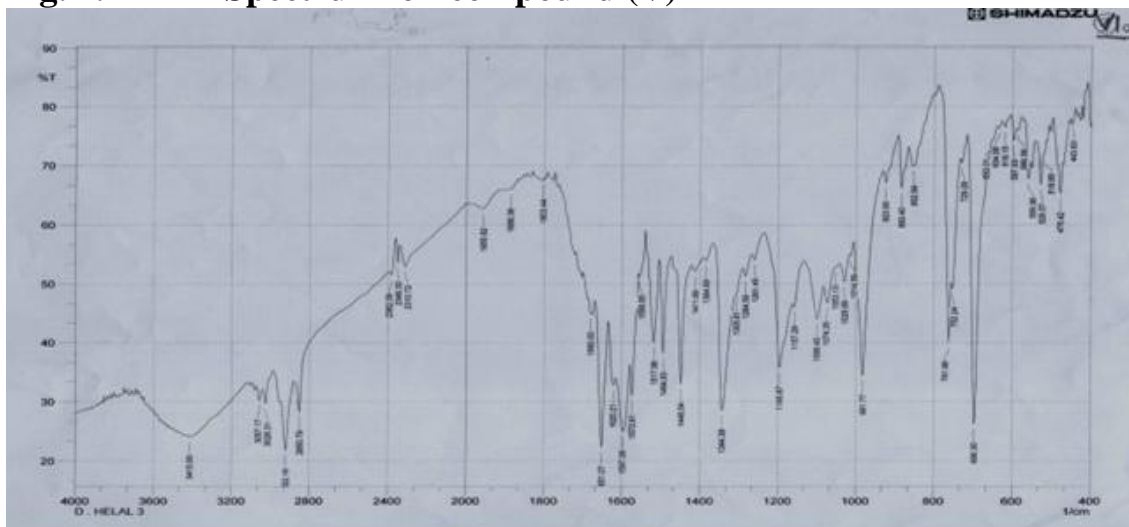


Fig. 5. FT-IR Spectrum of compound (VIa)

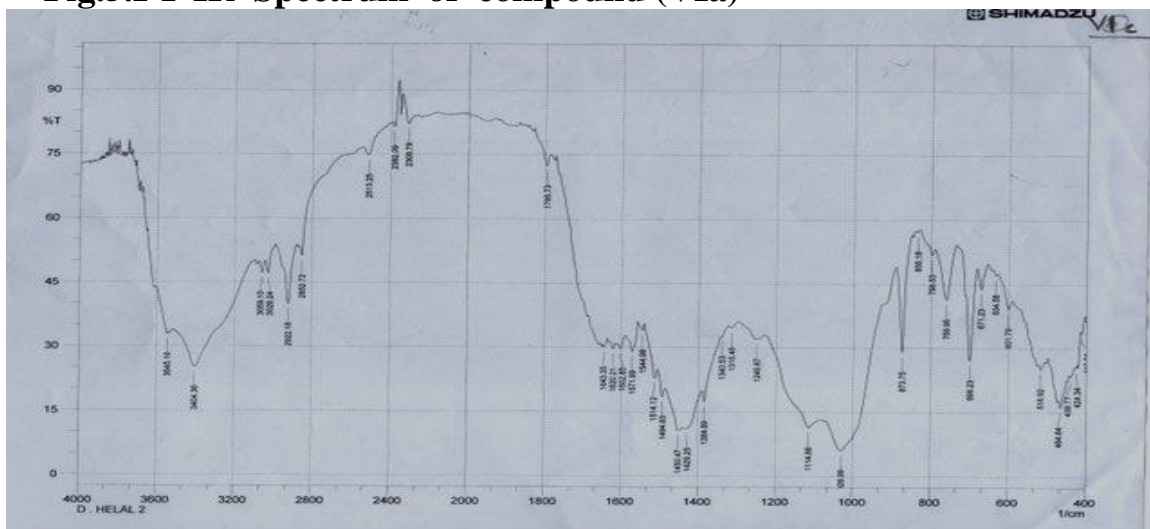


Fig. 6. FT-IR Spectrum of compound (VIb)

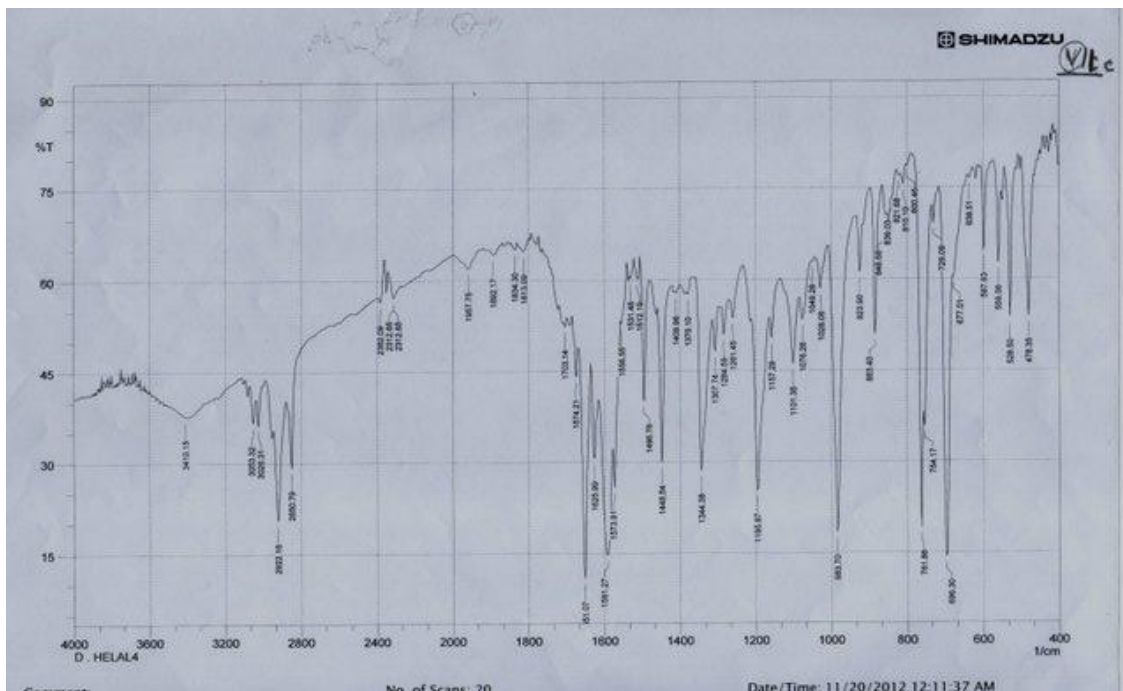


Fig. 7. FT-IR Spectrum of compound (VIc)

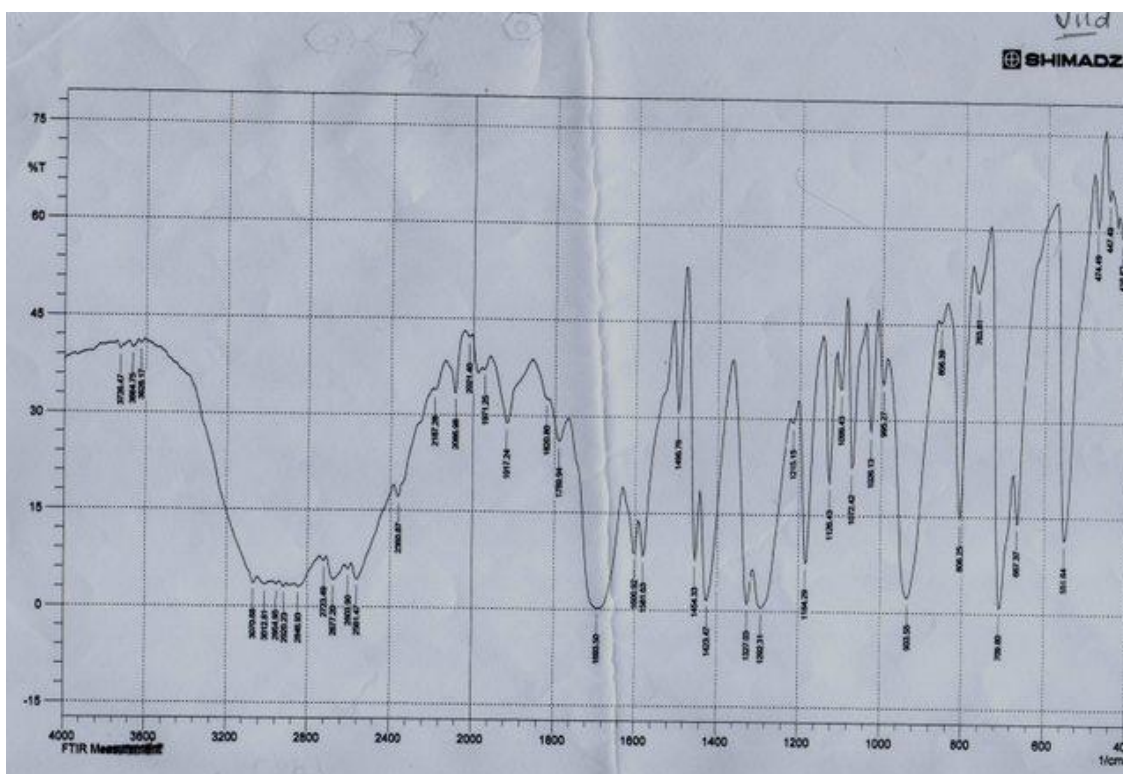


Fig. 8. FT-IR Spectrum of compound (VIId)

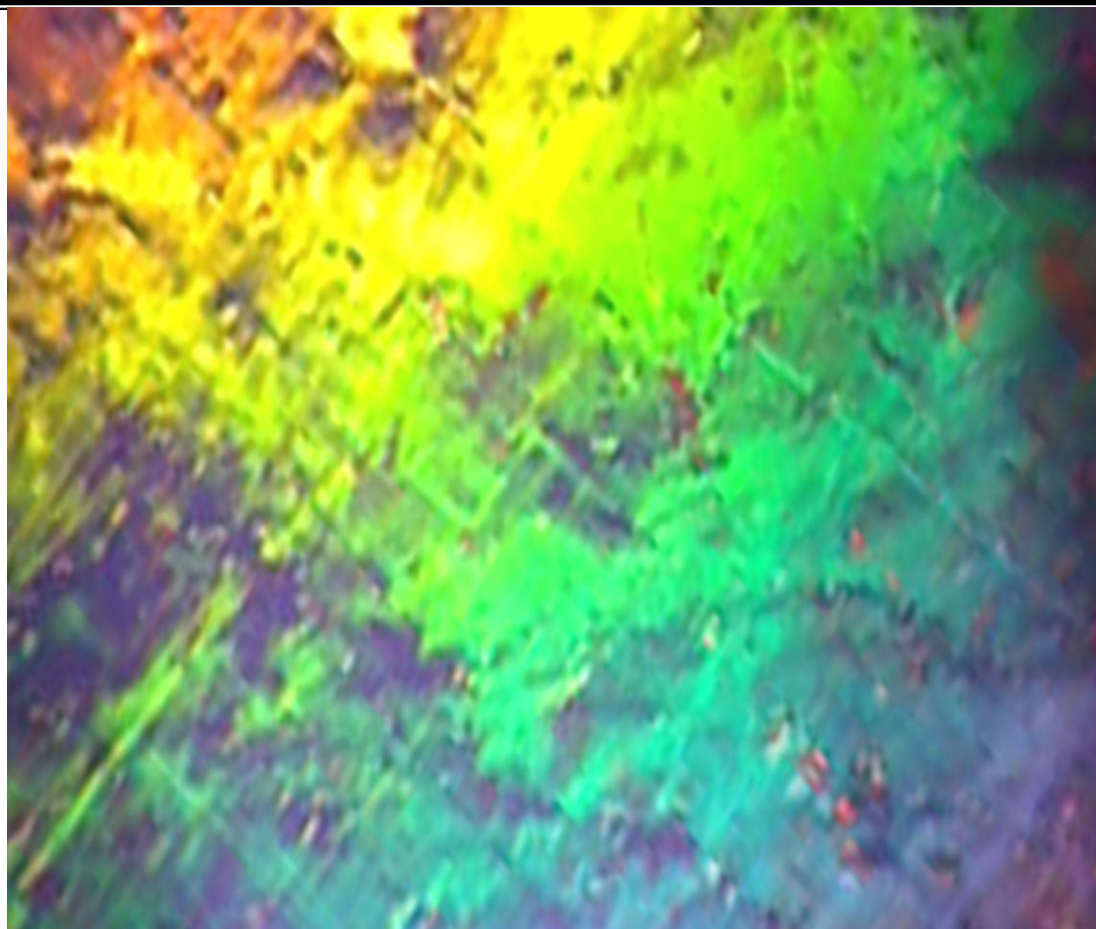


Fig-9-Smectic A texture of compound -VIIb at 120⁰ C

Conclusion

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

References

- [1] Oleg A. Rakitin, One-pot synthesis of sulfur heterocycles from simple organic substrates , ARKIVOC, 2009, Page 129.
- [2] Salat K, Moniczewski A, Librowski T. , Nitrogen oxygen or sulfur containing heterocyclic compounds as analgesic drugs used as modulators of the nitroxidative stress, Mini Rev Med Chem. 2013 Mar;13(3):335-52.
- [3] Taghreed . H. Al-Noor , Ahmed .T.AL- Jeboori , Manhel Reemon Aziz, Preparation Characterization and Antimicrobial activities of {Fe(II),Co(II),Ni(II),Cu(II),and Zn(II)}Mixed Ligand Complexes Schiff base derived from Cephalixin drug and 4-(dimethylamino) benzaldehyde with Nicotinamide , Advances in Physics Theories and Applications 2013, Vol.18.
- [4] Sarika Verma, Sarita Shrivastva and Poonam Rani , Synthesis and spectroscopic studies of mixed ligand complexes of transition and inner transition metals with a substituted benzimidazole derivative and RNA bases, Journal of Chemical and Pharmaceutical Research, 2012, 4(1):693- 699.
- [5] Harris, J. M. Eds., Poly ethylene Glycol Chemistry, Biotechnological Applications; Plenum Press: New York, 1992.
- [6] Mazaahir Kidwai, Divya Bhatnagar, Ritika Chauhan, Potassium Carbonate-Mediated Green and Efficient Synthesis of Imidazo [2,1-b]-1,3,4-thiadiazoles Using PEG as Solvent, Journal of Heterocyclic Chemistry, 2013, Volume 50, Issue S1, pages E234–E236.
- [7] Harris, J. M.; Zalipsky, S. Polyethylene Glycol, Chemistry and Biological Application; ACS Books, 1997, Washington DC.
- [8] Mao, J.; Guo, J.; Fang, F.; Ji, S. –J., Tetrahedron, 2008, 64, 3905.
- [9] Mukhopadhyay, C.; Tapaswi, P. K. Tetrahedron Lett, 2008, 49, 6237.
- [10] Kouznetsov, V. V.; Merchan Arenas, D. R.; Bohorquez, A. R. R., Tetrahedron Letters, 2008, 49, 3097.
- [11] Santaniello, E.; Manzwchi, A.; Sozzani, P., Tetrahedron Letters. 1979, 20, 4581;
- [12] Brandstrom, A. Acta Chem Scand, 1956, 10, 1197.
- [13] Santaniello, E.; Ferraboschi, P.; Sozzani, P. Synthesis, 1980,646.
- [14] Hilal M. Abdullah, Abdul Wahid M. Abdullah & Taghreed H. Al-Noor, International Journal for Sciences and Technology, 2012, Vol. 7, No. 4, page 25.

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

- [15] Yelamaggad, C.V.; Shashikala, I.S.; Liao, G.; Rao, D.S.S.; Prasad, S.K.; Li, Q.; Jakli, A., Blue phase, smectic fluids and unprecedented sequences in liquid crystal dimers, Chem. Mater, 2006, 18, 6100-6102.
- [16] G.W.Gray and J.W. Goodby, Smectic Liquid Grystacls: Textyres and Structures, Leonard Hilm, London 1984.
- [17] Hioki, H.; Fukutaka, M.; Takahashi, H.; Kubo, M.; Matsushita, K.; Kodama, M.; Kubo, K.; Ideta, K.; Mori, A. Development of a new traceless aniline linker for solid-phase synthesis of azomethines. Application to parallel synthesis of a rod-shaped liquid crystalline library. Tetrahedron, 2005, 61, 10643-10651.
- [18] SPik Kwan, L., Dongzhong, C., Qingwei, M., Shing Wong, M., Highly ordered smectic phases from polar calix[4]arene derivatives. Chem. Mater, 2006, 18, 3924–3930.
- G. W. Gray and J. W. Goodby, Smectic Liquid Crystals: Textures and Structures, Leonard Hill, London, 1984.