Synthesis of Schiff'S Bases Derived from 2-Amino -1,3,4-Thiadiazole and 1,3,4-Oxadiazole with Naphthaldehydes

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Abstract

Two series of compounds were synthesized,the first one containing heterocyclic ring (1,3,4 thiadiazole) with α/or- β-naphthaldehyde and the second one containing (1,3,4-oxadiazole) with different substituted benzaldehydes . These compounds are Schiff's bases derived from the reaction of 2-amino-5(p-substituted phenyl)1,3,4-thiadiazole (series one) with α/or- β- naphthaldehyde , while series two was derived from the reaction of 2-amino -5- (β-naphthyl) 1,3,4- oxadiazole with different substituted benzaldehydes . The structures of these compounds have been characterized by FT-IR , UV ,Mass spectra in addition to H^1NMR spectra for some of them .

Introduction

Many classes of heterocyclic compounds have been synthesized earlier , and tested for their biological activity , liquid crystalline properties and isolation of organic isomers [1-4].These compounds are derivatives of thiadiazoles , oxadiazoles and triazole[5] .

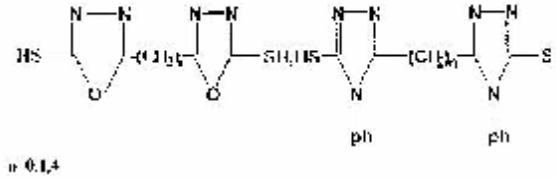
Pavluchenko et al.,[6] have prepared and studied the physical properties of 2,5 - disubstituted benzoxazole and benzthiazoles having structure (I).

X =O ,S

I

Y:(N=CH)

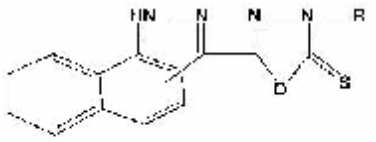
Other workers have synthesized a series of compounds ,which have shown to posses biological activity [7-8], including bis -oxazoles, thiadiazoles with aliphatic or aromatic groups as shown in structure (II).



n = 0,1,4

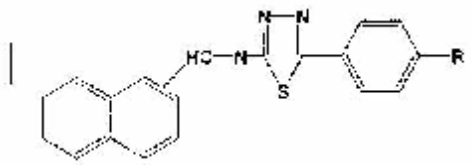
II

However, the effect of substituents on the biological activity is undoubtedly dependent upon the nature of substituents located on the molecules[9-13] having structure III.



III

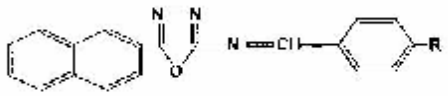
In the present work, we synthesized a series of heterocyclic compounds, that is 2-(N-α/or β-naphthylidene amino)-5-[p-substituted phenyl]-1,3,4 thiadiazole from the reaction between suitable naphthaldehyde and 2-amino 1,3,4-thiadiazole, having structure (IV).



SERIES 1 R=

IV

The second series includes Schiff bases from the reaction between 2-amino oxadiazole, which substituted with naphthyl ring and different substituted benzaldehydes having the structure (V)



V

Series 2. R= H , OH ,NO_2 , $N(CH_3)_2$, Cl , CH_3 ,3,4-di OH.

2-(N-p-substituted benzylidene amino)-5-[β-Naphthyl]-1,3,4-oxadiazole

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Experimental

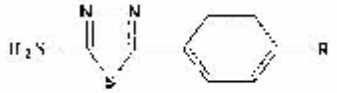
Materials :p-substituted benzoic acids and α/or β naphthaldehyde were BDH analar grade .Solvents and other chemicals used of analar grade. Melting points were determined on Electrothermal melting point apparatus and are uncorrected.

The FT.IR spectra were recorded on a Pye-Unicam spectrophotometer as KBr disk in the 4000-500 cm^{-1} range .Mass spectra were recorded on a Perkin Elmer (ADMS9) spectrophotometer, UV spectra were recorded on a shimadzom spectrophotometer ,H^1NMR(for some of the prepared compounds) were recorded on a Varian 360 MHz instrument at Sussex university /u.k .

The synthesis

Series 1

1-Preparation of [2-(N-α-Naphthylidene amino)-5-[p-substituted pheayl]-1,3,4-triadiazole .



R p-OCH_3, p OC_2H_5, p Cl, p F, p I

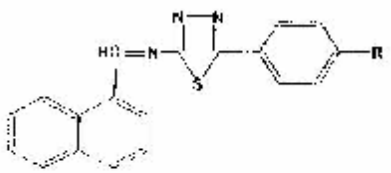
VI

A mixture of p substituted benzoic acid (0.01 mole), thiosemicarbazid (0.01 mole) and phosphorus oxy chloride (5ml.)was heated under reflux for (4) hours .The mixture was cooled and diluted with water ,then refluxed for further one hour . After that , the reaction mixture was filtered and the filtrate neutralized with potassium hydroxide to give white precipitate .The precipitate was washed with distilled water and re-crystallized from (mix 50:50 ethanol : water) to give the desired thiadiazole with yield and melting points as follow :

Table (1): **Physical properties of compounds VI.**

Comp.No.	R	M.P. °C	Yield .%
VIa	OCH_3	190	90
VIb	OC_2H_5	>250	85
VIc	Cl	>250	85
VId	F	>250	90
VIe	I	>250	90

2-Preparation of 2-(N-α-Naphthylidene amino)-5-[p-substituted phenyl]-1,3,4-thiadiazole.



SERIES 2 R=p-I, p Cl, p F, p OCH_3, p- OC_2H_5

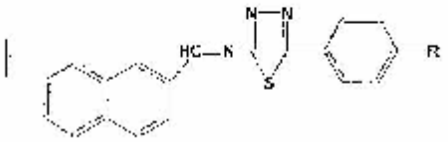
IV

A mixture of 2-amino- 5- (p-substituted phenyl) -1,3,4-thiadiazole (0.01 mole) in absolute ethanol (20 ml.) and α naphthaldehyde (0.01mole) with (1-3) drops of glacial acetic acid was refluxed for(1) hour with continuous stirring .The reaction mixture was cooled to room temperature for half an hour to give a yellow precipitate .The precipitate was filtered ,dried in vacuum oven overnight and re crystallized from ethanol to produce the desired compound with yield and melting point as follow:

Table (2): Physical properties of compounds VI .

Comp.No.	R	M.P.°C	Yield %
VIa	I	150	80
VIb	Cl	175	80
VIc	F	160	85
VId	OCH_3	132	95
VIe	OC_2H_5	100	80

3-Preparation of 2-(N-β-Naphthylidene amino) 5-[p-substituted phenyl]-1,3,4-thiadiazole.



SERIES 1 R=I,Cl,F,OCH_3,OC_2H_5

VII

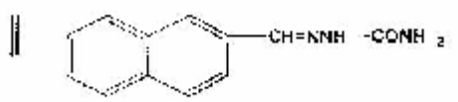
Procedure(2) was followed for the synthesis of these compounds under the same conditions ,the melting points and yield as follow :

Table (3): Physical properties of compounds VII .

Comp.No.	R	M.P.°C	Yield %
VIIa	I	125	75
VIIb	Cl	130	70
VIIc	I	175	80
VIId	OCH_3	153-155	90
VIIe	OC_2H_5	70	80

Series 2:

1-Preparation of[β-naphthaldehyde semicarbazone]VIII.



VIII

A mixture of semicarbazide hydrochloride (0.0089 mole) fused sodium acetate (0.0.8mole) in (10ml) ethanol and a solution of β-

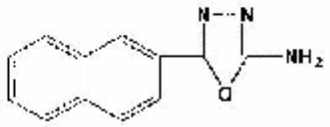
naphthaldehyde (0.0064mole) in (10ml EtOH) was refluxed with constant stirring for about 40 minutes. The reaction mixture was allowed to cool to room temperature and poured in distilled water (50 ml.) .The white solid precipitate was filtered and re-crystallized from glacial acetic acid with melting point (230 C^0) and yield = 90 %.

(spectral aspect of the semicarbazones)

U.V (MeOH) :λ max 270 nm.

IR:ν(3450 NH_2),3150(NH),1665(-$CONH_2$)cm^{-1}.

2-Preparation of [2-amino-5-(β –naphthyl) 1,3,4-oxadiazole].



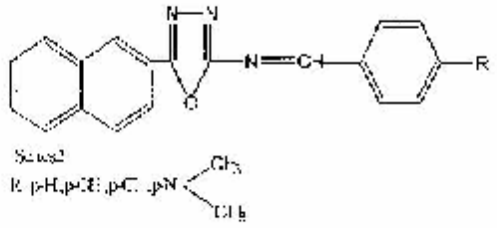
IX

A solution of bromine (0.6ml) in acetic acid (5ml) was added to stirred slurry of β-naphthaldehyde semicarbazone VIII (0.0087mole) with anhydrous sodium acetate (0.049mole) in acetic acid (5ml) as solvent .The reaction mixture was cooled in ice bath to 0^0C temperature for 10 minutes to give faded orange precipitate .The product was dried in oven overnight with melting point (195^0 C)and yield =85%.

UV (MeOH) : λ max 280 nm ,Ɛ max 1.85 .

IR :ν 3350-3100 (-NH_2) , 1040 (O-C-O-),1610 (C=N) cm^{-1}.

3-Preparation of 2-(N-p-substituted benzylidene amino) 5-(β-Naphthyl)-1,3,4-oxadiazole.



V

A mixture of 2-amino-5-naphthyl 1,3,4-oxadiazole (0.01mole) in absolute ethanol (15ml) as a solvent and p-substituted benzaldehyde (0.01mole) with (2-3)drops of glacial acetic acid was refluxed for one hour with continuous stirring .The reaction mixture was cooled to room temperature to give a yellow precipitate .The precipitate was filtered , dried in vacuum oven for overnight and re-crystallized from ethanol to produce the desired compound ,with yield and melting point as follow:

Table (4):Physical properties of compounds V .

Comp.No.	R	M.P. ^{0}C	Yield %
Va($C_{19}H_{13}N_3O_2$)	OH	100	80
Vb($C_{19}H_{12}N_4O_3$)	NO_2	223	85
Vc($C_{19}H_{12}N_3O_3$)	3,4-di OH	>240	80
Vd($C_{19}H_{13}N_3O$)	H	120	70
Ve($C_{21}H_{18}N_4O$)	$N(CH_3)_2$	240	70
Vf($C_{19}H_{12}N_3OCl$)	Cl	210	70
Vg($C_{20}H_{15}N_3O$)	CH_3	160	85

Results and Discussions

1-Characterization of [2-amino -5-(p-Methoxy,Ethoxy,Flouro,Chloro and Iodo phenyl) 1,3,4 thiadiazole] VI.

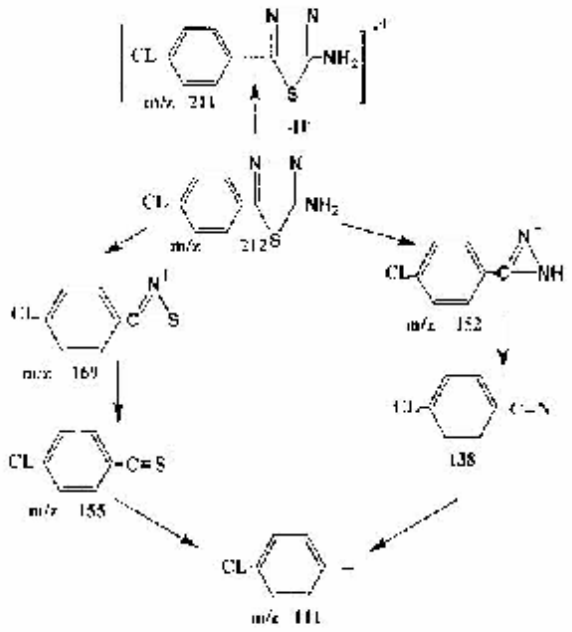
The reaction of thiosemicarbazide with the appropriate p-substituted benzoic acid in presence of phosphorus oxychloride afforded 2-amino-5-(p-substituted phenyl) 1,3,4-thiadiazole.

The FT-IR spectra of these compounds [VI] in general ,exhibited significant two bands in the region (3251-3097) cm^{-1}, which could be attributed to asymmetric and symmetric stretching vibration of NH_2 group. In addition to a band at about 1610 cm^{-1} due to cyclic (C=N)stretching is also observed .The spectra also displayed an a symmetrical C-O-C (aromatic) stretching band at (1250-1252) cm^{-1} ,with symmetrical stretching near 1080 cm^{-1}, in addition to a peak at 837 cm^{-1},due to p substituted group as shown in Figs(1-4) .

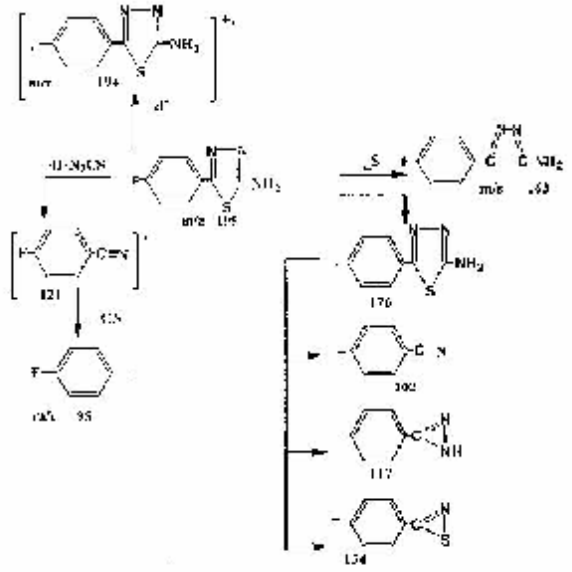
UV spectra Figs (5-7) show the transions $n\rightarrow\pi$ and $\pi\rightarrow\pi^*$ which confirmed the presence of the un bonded pair of electrons on sulfur atom and aromatic system (double bond).

Mass spectra Figs (8,9) of the compounds(VIc,VId) exhibit prominent molecular ion at 272 m/z and at 195 m/z ,respectively which corresponds to the molecular weight of both compounds. According to these data the expected molecular formula of these compounds are $C_8H_6N_2SCl$, $C_8H_6N_2SF$.

The fragmentation of the compound (VIc,VId) (as example) can be illustrated by the following mechanism :



Scheme 1.Fragmentation pattern of compound VIc.



Scheme 2.Fragmentation of compound VId .

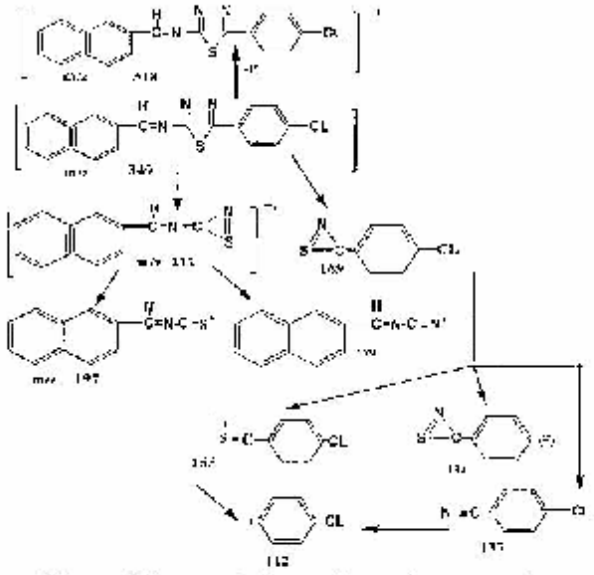
Scheme 1,2 represent the fragmentation rout specific to compounds[VIc,d],the mass spectra of these compounds gave the molecular ion at m/z 212 ,195 which are equal to molecular weight of the structures given to these compounds ,Figs (8,9) ,the most informative fragments obtained in the mass spectra are illustrated in Schemes 1,2.

2-Characterization of 2-(N-α-Naphthylidene amino)-5-[p-substituted phenyl]-1,3,4-thiadiazole .

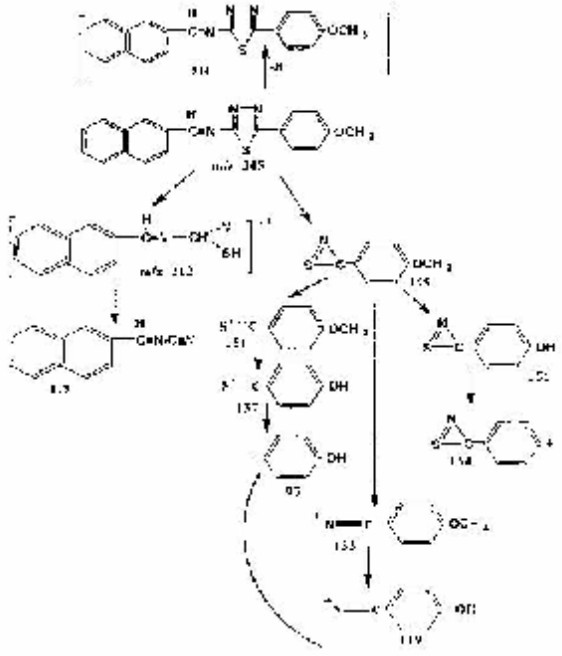
The Shiff bases were synthesized from the reaction between 2-amino 5-(p-substituted phenyl)1,3,4-thiadiazole and α or /β-naphthaldehyde.

The synthesized compounds were characterized by IR , Mass and H^1NMR spectra . The characteristic IR absorption bands Figs (10 12) , as examples , show the disappearance of two absorption bands due to (NH_2) stretching of amino thiadiazole at 3500 cm^{-1} and appearance of C=N absorption band at 1600 cm^{-1}.

Mass spectra Figs(13-15),exhibit prominent molecular ion at (344m/z) for compound(IVd).(α$C_{20}H_{12}N_3SO$), at (348m/z) for compound (VIIb),(β $C_{19}H_{13}N_3SCl$) and at 347m/z) for compound (VIId),(β-$C_{20}H_{12}N_2SO$),Scheme (3,4).



.Scheme 3.Fragmentation pattern of compound VIIb.



Scheme 4 ,Fragmentation pattern of compound VIId.

Mass spectrum of compound [15] ,Fig (15),exhibited prominent molecular ion at m/z 345,which corresponds to the molecular weight of structure assigned to this compound .The molecular ion losses a mass of 133 to give the cation 2 at m/z 212 which subsequently undergoes another fragmentation Scheme (2).The most important step in this Scheme is the loss of fragment H_2N_2CS from the molecular ion giving rise to the radical cation 2 at m/z 179 .The presence of two peaks at m/z 139 and m/z 151 is an indication that a 1,3,4-thiadiazole ring is present

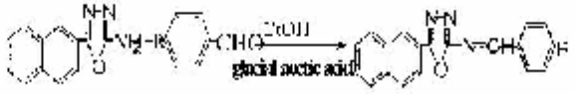
The H NMR spectra of some compounds show the expected peaks for all protons Figs(16-18).

H^1 NMR (CD_3Cl-300MHZ) for compound (IVd) Fig. (16), 3.80 (s, 3H , OCH_3) . 5 (s,1H,CH).7-7.1(d,2H,Ar-H) , 7.8 for para phenyl substitution and other peaks (7.2-7.7) etc.,for naphthalene ring.

Also 3.8-4(s,1H,CH) ,7-8(m,Ar-H) for phenyl ring ,8-8.2(d,2H,Ar-H) for naphthyl ring) for compound (VIIb),(β $C_{19}H_{12}N_2SCl$) Fig (18).

The UV spectrum Fig (19) confirmed the structure of the prepared compound (VIId).

3-Characterization of [p-substituted benzylidene -2-N (imino)1,3,4-oxadiazole-5-β-naphthyl] .



Va-g

The characteristic IR absorption bands show the disappearance of absorption bands for NH_2 of amino oxadiazole at 3500 cm^{-1} , the appearance of (C=N) absorption band at 1600-1650 cm^{-1} with absorption bands at 1080-1100 cm^{-1}due to para substitution .The IR spectral data of the synthesized compounds are given in Table (5).

Table (5) :IR spectra bands of the Schiff bases of series II:

Comp. No.	C=N	C=C Ar	C-R
Va	1630	1510-1610	830-850 (OH)
Vb	1640	1600	$-(NO_2)$
Vc	1630	1605	-(di OH)
Vd	1650	1610	-(H)
Ve	1635	1610	840N$(CH_3)_2$
Vf	1630	1610	-Cl
Vg	1640	1600	$=CH_3$

Furthermore, it appears that the donating groups exhibited decrease in melting points, whereas withdrawing groups exhibited increase in their melting points .These results are in good agreement with previously work[19] . That may be attributed to the fact that, the donating groups decrease the polarity of the molecule while withdrawing groups increase the polarity.

Conclusion

Various substituted heterocyclic compounds were synthesized and characterized by different spectroscopic technique, in attention to investigate their biological or industrial (as a dyes) activity.

References

1-M. Sato ,T.Yoshinaga and N. Koide, Polymer Journal vol. 32,Iss 9,pp 753-759 (2000).

2- D. Gomes, CP. Borges and J.C. Pinto, Polymer vol, 42. Iss 3 pp 851-865 (2001)

3-YM. Sun and CS. Wang. Polymer vol 42,Iss 3 pp 1035-1045 (2001)

4- HW. Zhao and WT.Hua, Synthetic communications vol 30, Iss 16,pp 2923-2931 (2000)

5- M. Abdel kader ,M.Eid Mohga and S.A.M.khalil Naser,Molecules 8, 744-755 (2003)

6- A.G.Ksmailor and B.A.salmoco ; Zh org khim., 4, 85(1998)

7- V.K. Mishra and S.C. Bahel, J. Indian chem.. Soc., (1983) .

8- A. Zayed , J. Metr , and S. El-hawary ; Egypt J.Chem 24 ,No. 5,389-396 (1981)

9- EA. Bakhite, AA-Geies and HS Elkashef, phosphorus sulfur and silicon and related Elements vol 157, pp 107—122 (2000)

10 MMH. Ariel, Revue Roumaine de chimie vol 44, Iss 2. pp 173-179 (1999).

11- H. Zasch. Wiss. Z. Martin, Luther Univ. Hal Wittenberg. Math-Naturwiss.. Reihe 29, 35 (1980).

12- M. Parra, S.Hernandez, J. Belmar Ye. Zuniga, Bol. Soc. (chile),Quim., 42, 507-518 (1997).

13- M. Parra G. Fuentes, V. Vera, SH. Villouta, S. Hernandez, Bol. Soc. Chili 49, 455-460 (1995).

14- Y., Kaminorz, B, Schulz and L, Brehmer, Synthetic Metals vol 111,Iss Jun, pp 75-78(2000).

15- Silverstein B. and Morrill,Spectrometric Identification of Organic Compounds, Fourth Edition (1980).

16- S.S. Parmar , M. Chaudhary, S K., Chaudhary, S., Kumar,H.R., Spiro, J. Pharm. SC.66,971 (1977).

17- J Mohan,Indian,J. Chem, 22B, 270 (1983).

18- N.K.Chudgar, S.N.Shah and R.A. Vora , Mo.Cryst. Liq. Cryst, Vol.172 ,pp 51-56 (1989).

19 K Ibtisam jassim ,H.gazwan AL. sonaidai and I. Yousif ;Tikrit Journal for pure science Vol 9.No. 2 ,166-170.(2003).

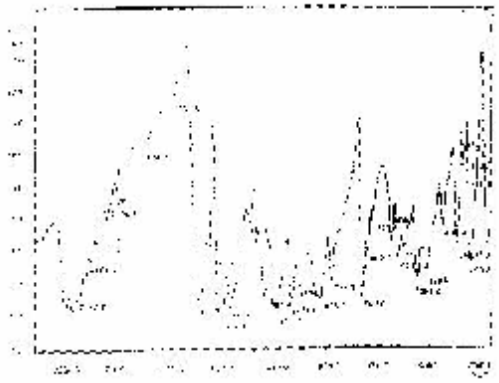


Fig (1) :FT-IR spectrum of compound (VIa) .

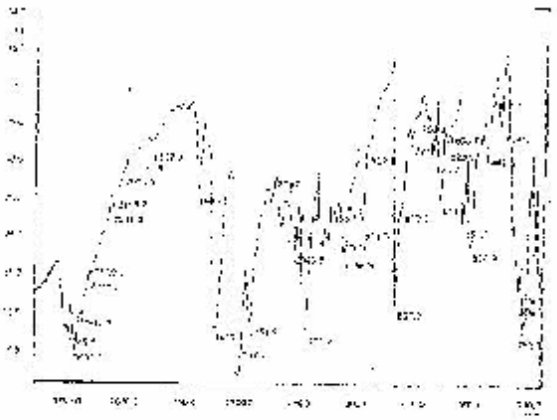


Fig (4) FT-IR spectrum of compound (VId) .

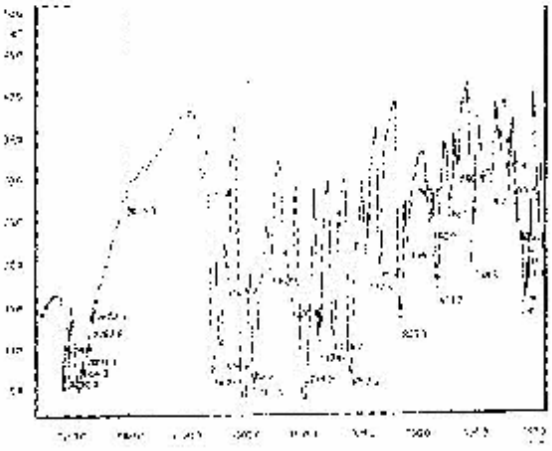


Fig (2) : FT-IRspectrum of compound (VIb).

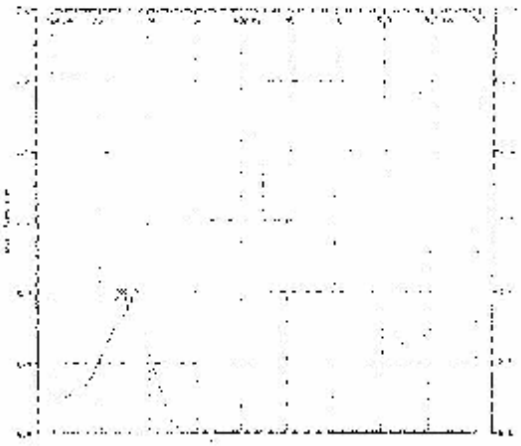


Fig (5) :UVspectrum of compound (VIb) .

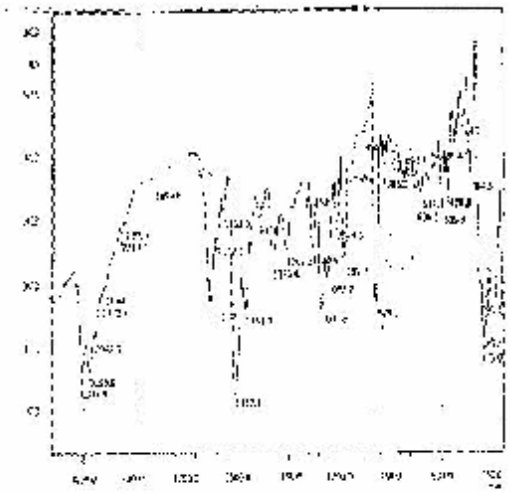


Fig (3) :FT-IR spectrum of compound (VIc) .

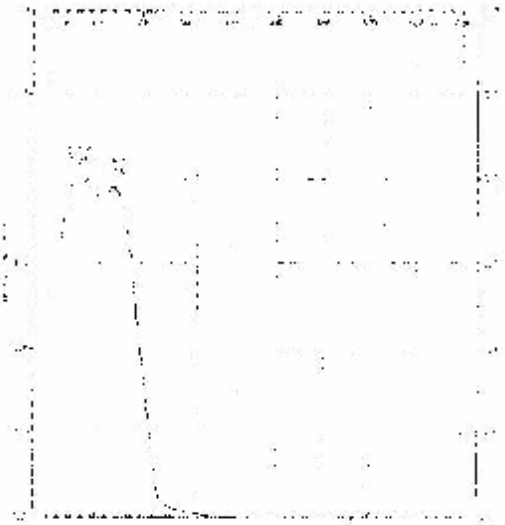


Fig (6) uv spectrum of compound (VIc)

Fig (7) :UV spectrum of compound (VId) .

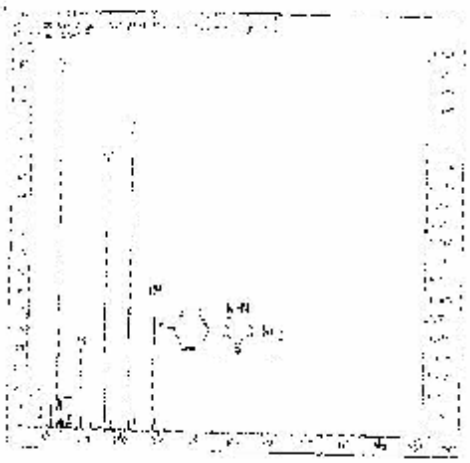


Fig (8) :Mass spectrum of compound (VId) .

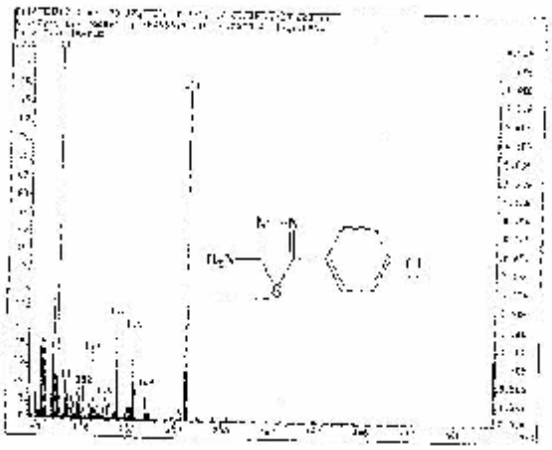


Fig (9) :Mass spectrum of compound (VIc) .

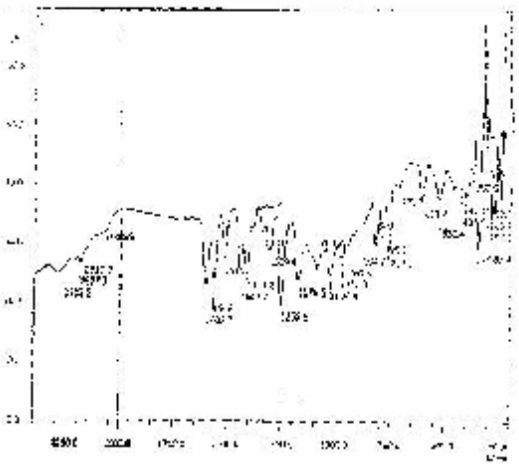


Fig (10) : FT-IR spectrum of compound (IVd) .

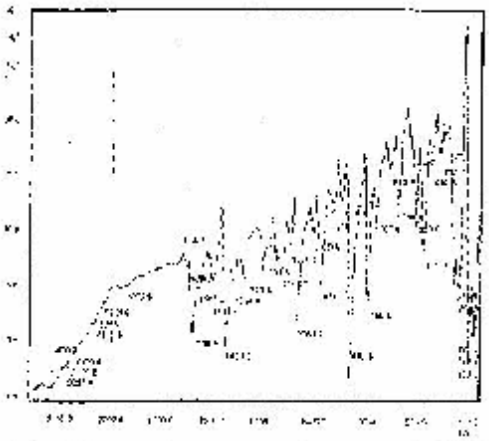


Fig (11) FT-IR spectrum of compound (VIb)

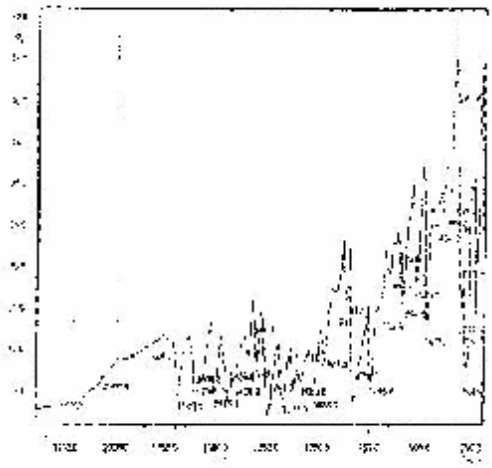


Fig (12) :FT-IR spectrum of compound (VIId) .

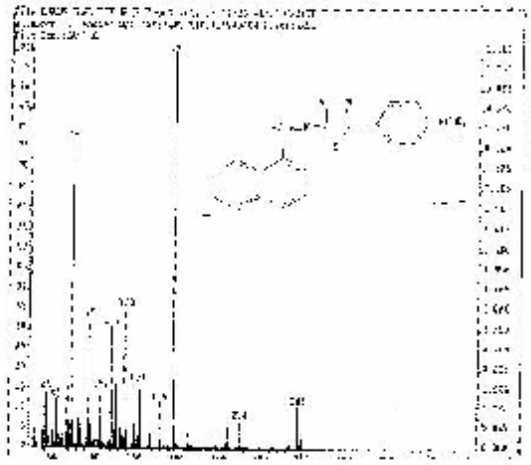


Fig (13) :Mass spectrum of compound (IVd) .

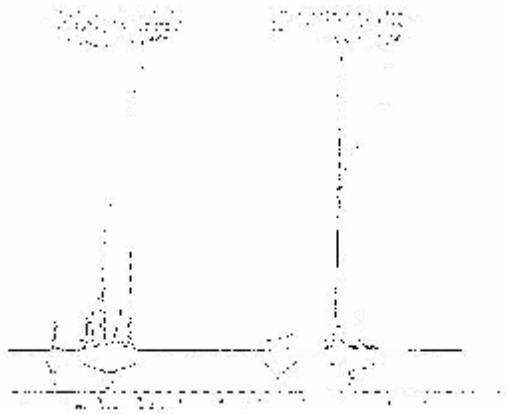


Fig (16) : H^1 NMR spectrum of compound (IVn)

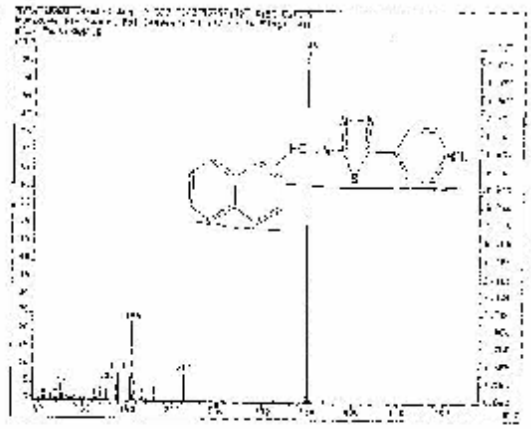


Fig (14) :Mass spectrum of compound (VIIb) .

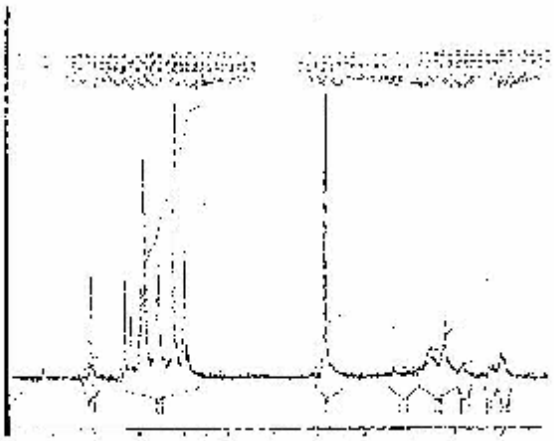


Fig (17): H^1NMR spectrum of compound (VIIa)

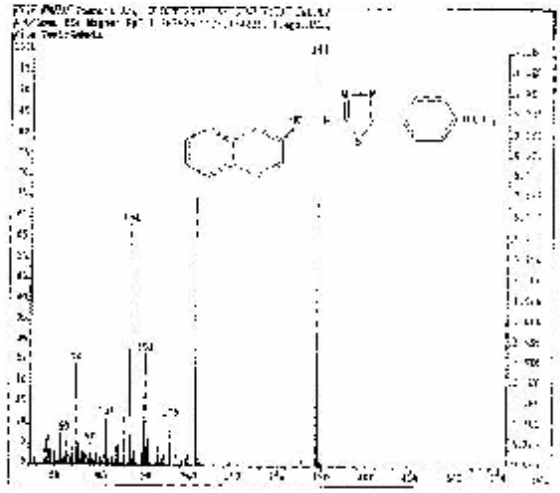


Fig (15) : Mass spectrum of compound (VIId) .

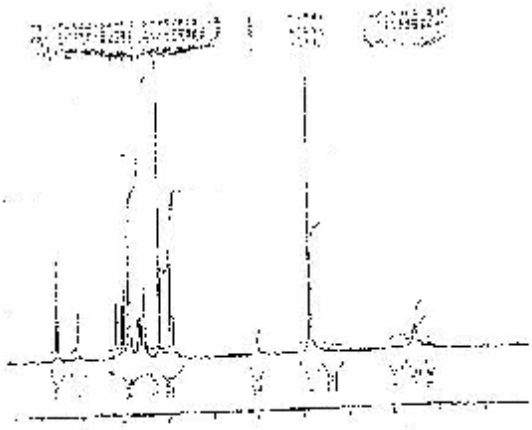


Fig (18) :H^1NMR spectrum of compound (VIIe)