Synthesis and Characterization of New phenolic Schiff bases Derivatives Based on Terephthaladehyde

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Abstract

A variety of new phenolic Schiff bases derivatives have been synthesized starting from Terephthaladehyde compound, all proposed structures were supported by FTIR, ^{1}H-NMR, ^{13}C-NMR, Elemental analysis, some derivatives evaluated by Thermal analysis (TGA).

Key words: Terephthaladehyde ,Fused epoxy ,Phenolic Schiff bases

Introduction :

The development of simple synthetic routes to widely used organic compound using readily available reagent is one of the main objectives of organic synthesis.

The use of Schiff base covered a wide area application in industry and biological field [1,2], the industry phenolic Schiff bases were used as a rubber accelerators [3], antioxidants and corrosion inhibitors [4], they have a wide industrial application as photo stabilizer's for poly ethylene, in analytical chemistry Schiff bases were used for uptake metal ion[5] some Schiff bases are used in the accurate determination for trace elements in the dilute solution, which is often hindered due to the sensitivity[6] limites of the equipment used for the purpose[6] in the study number of epoxy Schiff bases[7] were prepared.

Material and Methods:

General

Melting points were determined on Gallen kamp, melting point apparatus and were uncorrected, FTIR spectra of the compounds were recorded on a (SHIMADZU) FTIR – 8300 spectrometer as KBr-disc, ^{1}H-NMR, ^{13}C-NMRspectra were recorded at 200.13 – 50.32MH$_{z}$, respectively using tetra methyl Silane (TMS) as an internal standard (DMSO) as solvent Elemental analyses were run using aperkin-Elmer, RE-2400 (C.H.N) analyzer, Thermal stability (TGA).

All analyses were formed in Center of Consultation / University of Jordan.

Materials

All the chemicals used were supplied by (Merk, Fluka and BDH) chemicals, the solvent purified by distillation and dries with calcium chloride .

Measurement and Techniques

The purity of products were investigated by (T.L.C) technique by using a mixture of benzene – ethanol (5:5 v/v) as eluate and Iodine champer for spot location

Thermal gravimetric analysis (:TGA)$^{(8)}$

Curing of the prepared epoxy Schiff bases resin were evaluated by using (NETZCH-ESTA) / 409-PG/PC) Mod/Type of Meas (DTA-TGA).

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The programmed heating rate of 20°C/min from (25-1000)°C under atmosphere (N_2 gas), so that heat lost or absorbed were recorded Fig.s (15-20) and analyzed Table (4).

Synthesis of[(1E,1E)-2-2-(2E-2E)-2-2-(1,4-phenylenen bis(methanylylidene))bis(hydrazine-1-yl-2-ylidene))diethenamine(1)[9]:

A mixture of (0.02 mol, 2.068gm) terephthaladehyde with (0.04 mol, 3.64gm) thiosemi carbazide in (25ml) abs. ethanol was refluxed for (6hrs), the solid formed and recrystallized from ethanol and used directly at the next step.

Synthesis5,5-(1,4-phenylene)bis(1,3,4-thiadiaz5l-2-amine)compoundwithcompoundwith ethane(1:1) (2)[10]:

A stirring solution (0.01mol, 2.86gm) of compound(1)
with (0.02mol, 9.6gm) Ammonium Iron III sulfate dehydrate (NH_4Fe $(SO_4)_2$. $12H_2O$) in (30ml) dis. Water was added and the refluxed continued for (4hrs) After cooling, the precipitate was collected by filtration and washed with dis. Water to give compound [2]. Recrystallizer by ethanol.

Synthesis (E)-4-(((1,3,4-thiadiazol-2-yl)imino)methyl)phenol compound with phenol and(E)-N—ethylidene-1,3,4-thiadiazol-2-amine and p-xylene and ethane(1:1:1:1:1)(3)[9]:

A mixture of (0.01mol, 2.76gm) compound [2] with (0.02mol, 2.44gm) p-hydroxy benzaldehyde in (25ml) abs. ethanol with (1-2) drops glacial acetic acid. Refluxing (6hrs) then cooled the precipitate and crystallized in THF.

Synthesis5,5(E)-4-(((1,3,4-thiadiazol-2-yl)imino)methoxye)oxarinec compound with oxarine and(E)-N-ethoxye-1,3,4-thiadiazol-2-amine and p-xylene and ethane(1:1:1:1:1)(4)[6]:

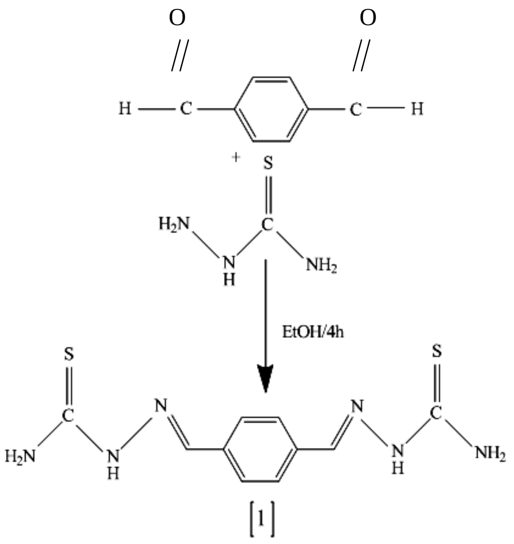
To a mixture of an appropriate (0.01 mol, 4.46gm) phenolic Schiff bases with (0.12mol, 11.1ml) eipchlorohydrine to (50°C) for (15min) was added gently alcoholic sodium hydroxide (0.14mol, 5.6gm) in two portions to keep the temperature below 65°C. The stirring was continued for (2h), after first addition the aqueous layer was separated from the organic layer, then the second portion of (NaOH) added and stirred for (1h) and left the mixture at the same temperature for 50min, and also the aqueous was separated, the organic layers were dried and excess of eipychlorohydrine and solvent distilled of under reduced pressure, the formed resins were purified by dissolving it in THF the filterization and evaporation of excess solvent at (50°C), the purified by thin layer chromatography (TLC).

Synthesis of epoxy phenolic Schiff bases with unstitched Ring (5-9)[8]:

A mixture of an appropriate (0.01mol, 5.96gm) compound [4] in (30ml) cold methanol and (0.02mol) secondary amine (piperidine, morpholine, 4-morpholine piperidine, 4-piperidino piperdine, 4-methyl piperdine, 1-methyl piperazine) respectively, refluxing for (72h), after cooling the solvent continued was avapourated and the residue purified by thin layer chromatography (TLC).

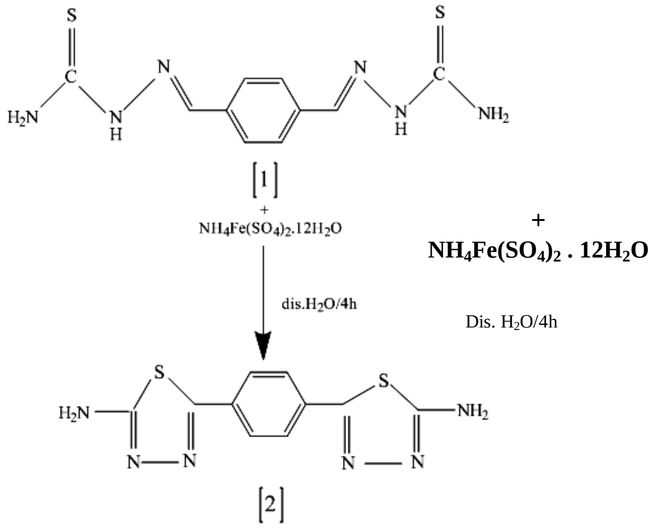
Results and Discussion :

Considerable interests have been expressed in Synthesis of Schiff bases in recent year due to their industrial and biological importance starting from.



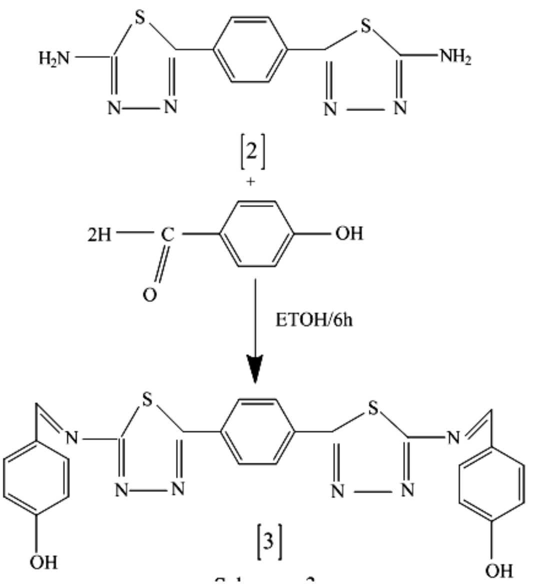
Scheme – 1 – Synthetic path ways for preparation of Compound (1)

In Scheme -1- out Line the Synthetic sequences employed in our laboratories for preparation of intermediate thiosemicarbazide, The FTIR Spectrum (11) showed the strong stretching vibration (3320)cm^{-1} due to (NH_2) , (3200)cm^{-1} for (NH), (1610)cm^{-1} for (C=N) , (1250)cm^{-1} for (C=S) , (3065)cm^{-1} for (Ar-H), ^{1}H-NMR (DMSO-d_6) δ: (7-7.9) ppm due to (Ar-H), (3.5-3.6)ppm due to (2H, NH_2), ^{13}C-NMR (DMSO-d_6) δ: (123-127)ppm due to aromatic carbones, (133)ppm due to(C=N), (162-169)ppm due to(C=S) , compound [2] prepared by the condensation of the corresponding compound [1] with Iron III ammonium sulfate $NH_4Fe(SO_4).12H_2O$. Refluxing in dis. Water



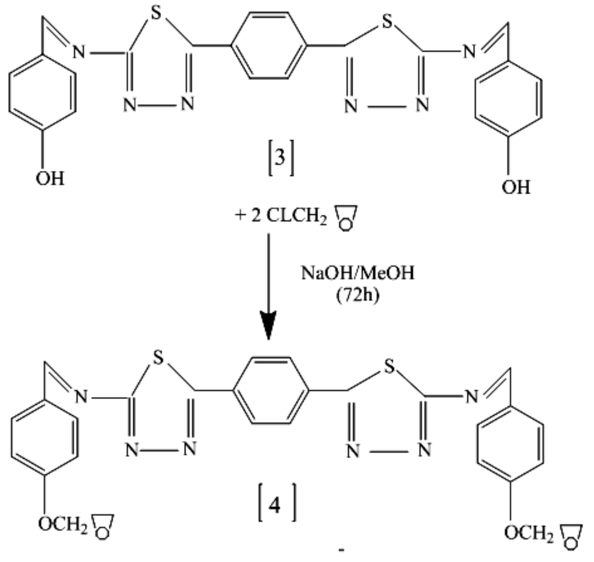
Scheme – 2 – Synthetic path ways for preparation of Compound (2)

The FTIR spectra showed strong stretching vibration (3400-3295)cm^{-1} for (NH_2), (3060)cm^{-1} fro (Ar-H)$_H$-NMR (DMSO-d_6) δ: (4.1-3.5)ppm due to (2H,NH2),(7.1-7.4)FOR (Ar-H); ^{13}C-NMR(DMSO-d_6): (131.4-135.1)ppm for aromatic carbon.(140)due to(Ar-NH_2) ,Phenolic Schiff bases prepared by condensation compound [2] with p-hydroxy benzaldehyde refluxing in abs. . ethanol



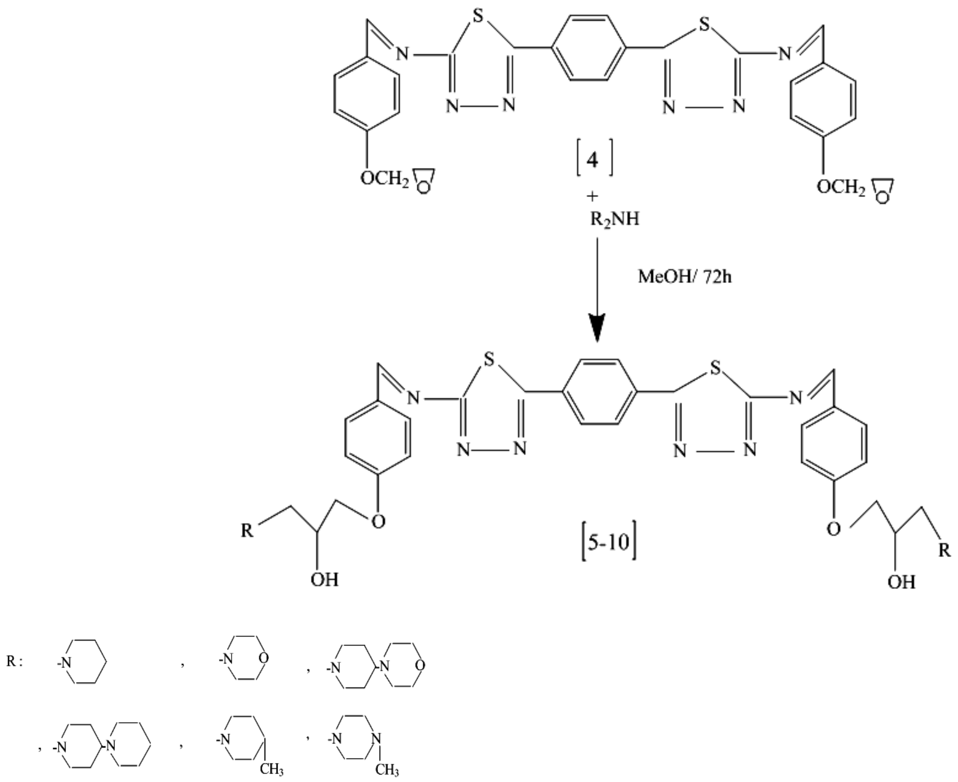
Scheme – 3 – Synthetic path ways for preparation of Compound (3)

FTIR spectra for compound (3) showed strong stretching vibration (1609-1612)cm^{-1} for (C=N) , (3410-3380)cm^{-1} for (OH) ,and (3100)cm^{-1} for (Ar-H); ^{1}H-NMR (DMSO-d$_6$) δ: (7.15-7.4)ppm for (Ar-H) , (10.1-10.3)ppm (H,OH), ^{13}C-NMR (DMSO-d$_6$) δ: (134-136)ppm for aromatic carbones. (164-165.2)ppm due to(C=N), (148.2-149.1)ppm due to (C ,OH).



Scheme – 4 – Synthetic path ways for preparation of Compound (4)

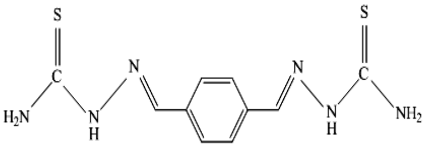
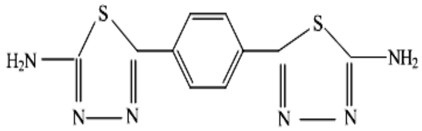
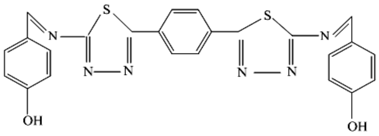
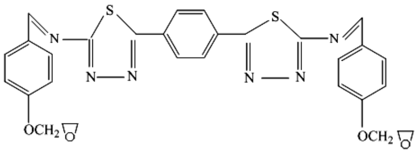
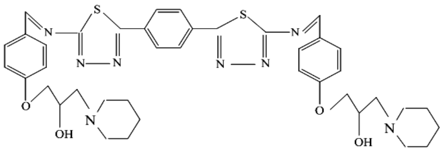
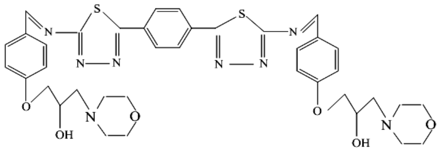
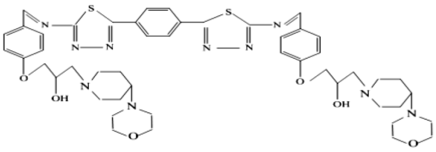
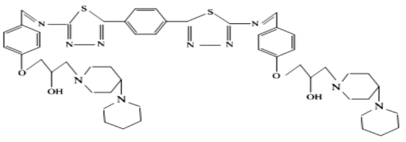
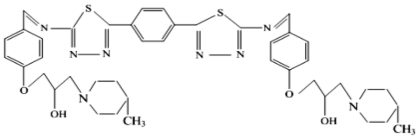
FTIR spectra for compound [4] obtained sharp band for (oxarine) absorption at (948-995)cm^{-1} , and strong bands (2931-2873)cm^{-1} for CH_2 , (1130-1090)cm^{-1} for (C-O-C).



Scheme – 5 – Synthetic path ways for preparation of Compound (5-10)

Finally compound [4] react with secondary amines (piperidine , morpholine, 4-morpholine piperidine, 4-piperidino piperidine, 4-methylpiperidine, 1 – methylpiperzine to gave unstitched ring (5-10). The FTIR spectrum of compound (5-10) obtained increasing in stretching vibration of alcoholic(OH) at (3350-3280)cm^{-1} and (1190)cm^{-1} for (C-O) ; ^{1}H-NMR (DMSO-d$_6$) δ: (6.7-7.4)ppm due to (Ar-H), (10.5)ppm for (H,OH); ^{13}C-NMR (DMSO-d$_6$) δ:(12.1-119)ppm due to aromatic carbones, (148-149)ppm for (C,OH)). All these steps were summarized in schemes (1-5).. physical properties and major FTIR absorption of all mentioned and other details [FTIR, Elemental analysis, TGA analysis; ^{1}H-NMR , ^{13}C-NMR] data are listed in table (1-4) respectively.Curing thermal stability of some compounds were evaluated by using (TGA) Table (4) clearly show the temperature rate belong to different type dissociated for derivatives Figs(15-20).

Table (1) Depacited physical properties and major (FTIR) absorption for (1-10) compounds

Comp No	Compound Structure	M.P °C	Colour	%yield	Major FTIR absorption		
					V_{OH}	$V_{C=N}$	other
1		<300	pale yellow	82	-	1610	VNH2 (3320) V_{NH} (3200) $V_{C=S}$ (1250) VAr-H (3065)
2		269-271	pale green	80	-	1646	V_{NH2} (3400) 3295 V_{Ar-H} (3060)
3		113-115	Orange	86	3410 3380	1609 1612	V_{Ar-H} (3100)
4		Oily	Brown	75	-		V_{CH2}(2931) 2873 V???(948) 995 V_{C-O-C} (1130) 1090
5		Oily	Brown	85	3350 3200	1635	V_{C-O} (1190) V_{C-O-C} (1109) V_{C-N} (1200)
6		Oily	Brown	85	3300 3290	1625	V_{C-O} (1160) $V_{(C-N)}$ (1195) V_{C-O-C} (1220)
7		Oily	Brown	80	3310 3291	1632	V-o$_{C-O}$ (1200) V_{C-N} (1230)
8		Oily	Brown	70	3306 3290	1630	V-o$_{C-O}$ (1111) V_{C-N} (1235)
9		Oily	Brown	70	3300 3287	1627	V_{C-O} (1182) V_{C-N} (1238)

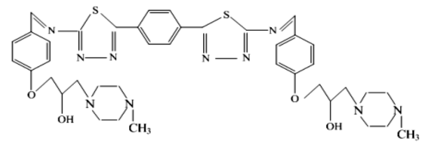
10		Oily	Brown	70	3309 3280	1631	V_{C-O} (1163) V_{C-N} (1250)

Table (2) Depacited, ^{1}H-NMR , ^{13}C-NMR for some compounds

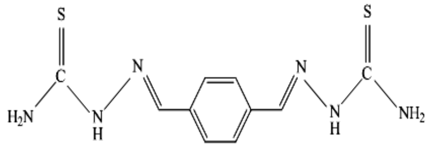
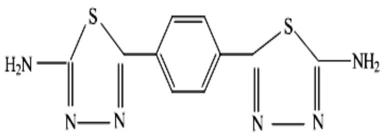
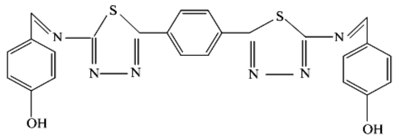
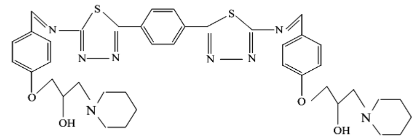
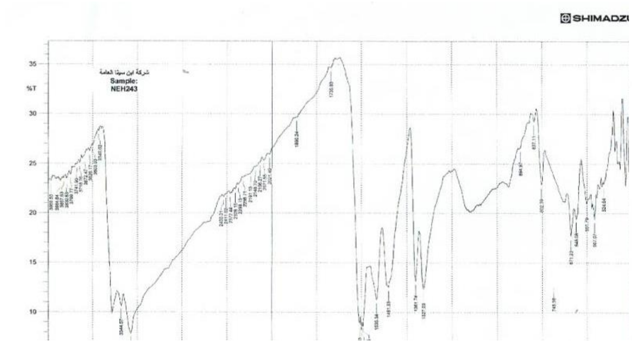
comp No	compound Structure	^{1}H-NMR	^{13}C-NMR
1		δ: 7-7.9 (Ar-H) δ: 3.5-3.6 (2H,NH_2)	δ: 123-127 (aromat. carb) δ: 133 (C=N) δ: 162-169 (C=S)
2		δ: 4.1-3.5 (2H,NH_2) δ: 7.1-7.4 (Ar-H)	δ: 1314-135.1 (aromat. carb) δ: 140 (Ar-NH_2)
3		δ: 7.15-7.4 (Ar-H) δ: 10.1-10.3 (H,OH)	δ: 134-136 (aromat. carb) δ: 164-165.2 (C=N) δ: 148.2-149.1 (C,OH)
5		δ: 6.7-7.4 (Ar-H) δ: 10.5 (H,OH)	δ: 124-129 (aromat. carb) δ: 148-149 (C,OH)

Table (3) Elemental analysis for some compounds

comp No	(C.H.N) analysis Calculated (Found)			comp No	(C.H.N) analysis Calculated (Found)		
	%C	%H	%N		%C	%H	%N
1	42.86 (43.86)	4.29 (5.27)	30 (30.9)	6	59.22 (60.02)	5.45 (6.23)	14.55 (15.50)
2	43.48 (44.45)	2.90 (3.89)	23.19 (24.19)	7	61.41 (62.32)	6.61 (7.40)	14.93 (15.71)
3	63.72 (64.70)	3.52 (4.50)	14.16 (15.16)	8	64.24 (65.20)	7.07 (7.90)	15.00 (15.75)
4	56.93 (57.93)	4.43 (5.40)	15.50 (16.32)	9	63.64 (64.40)	6.06 (7.02)	14.14 (14.98)
5	65.40 (66.32)	6.27 (7.19)	15.26 (16.24)	10	62.42 (63.21)	6.24 (7.11)	18.21 (18.96)

Table (4) Show Curing temperature of some compounds

comp No	primary dissociated	Finally dissociated	50% dissociated	maximum dissociated	average dissociated	%char content
4	220	380	350	310	0.25	93.77
5	210	475	350	275	0.16	83.97
6	190	525	370	325	0.96	79.44
8	180	750	612	325	0.069	61.63
9	120	700	647	425	0.054	59.94
10	165 260	700	660	360	0.053	58.70



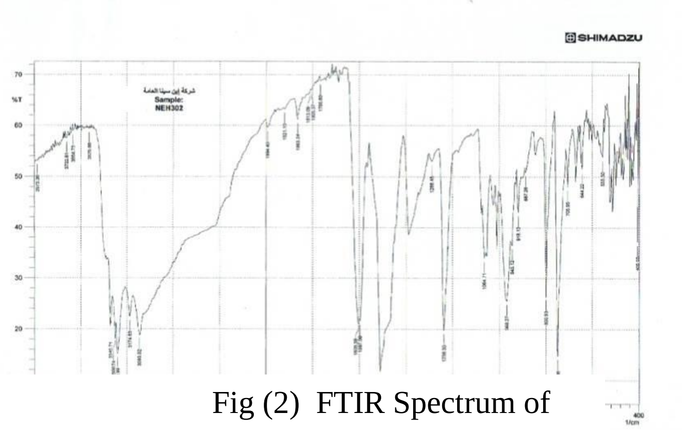
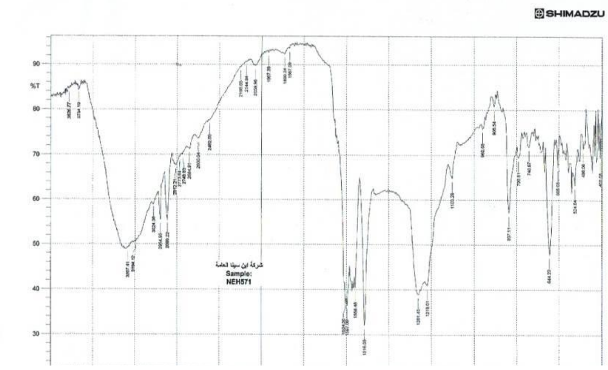


Fig (1) FTIR Spectrum of Compound (6) Fig (2) FTIR Spectrum of
Compound (4)



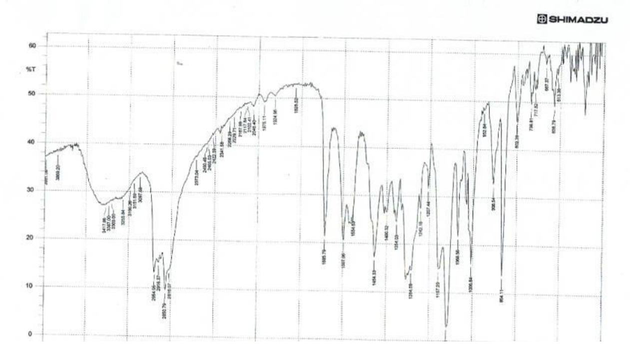
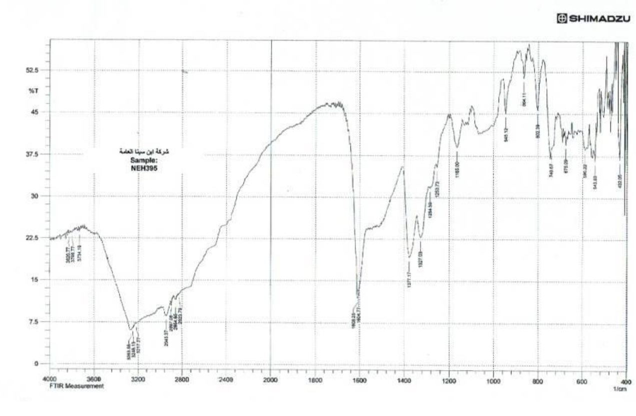


Fig (3) FTIR Spectrum of Compound (6) Fig (4) FTIR Spectrum of
Compound (8)



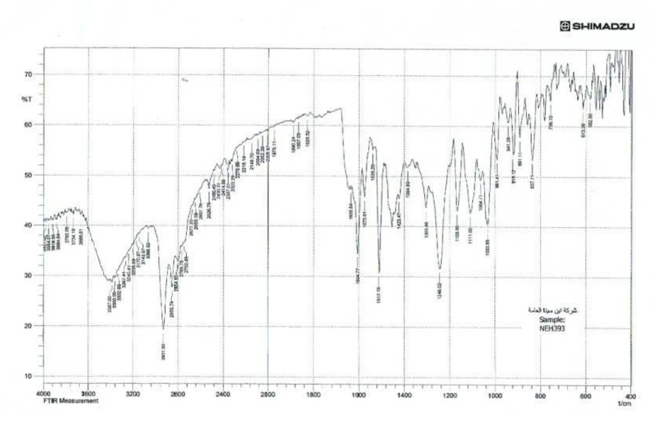


Fig (5) FTIR Spectrum of Compound (9) Fig (6) FTIR Spectrum of
Compound (10)

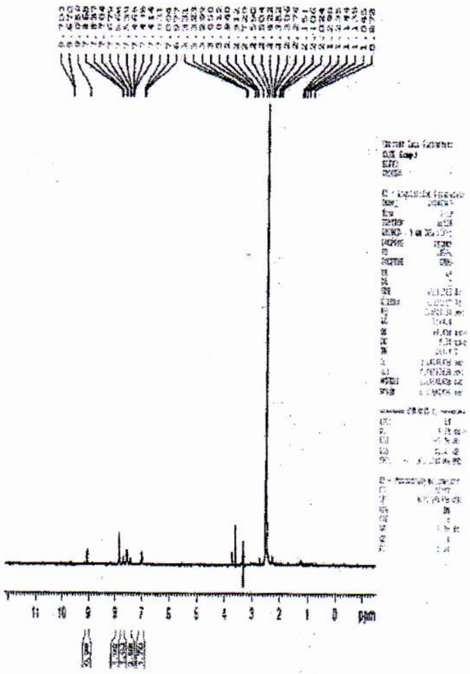


Fig (7) HNMR Spectrum of Compound (1)

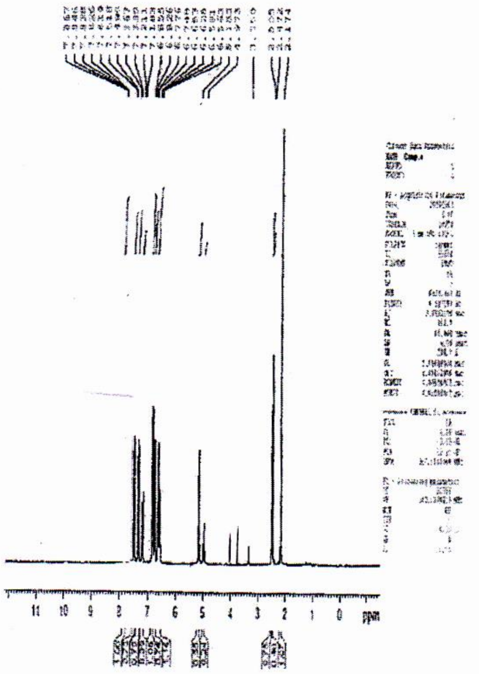


Fig (8) HNMR Spectrum of Compound (2)

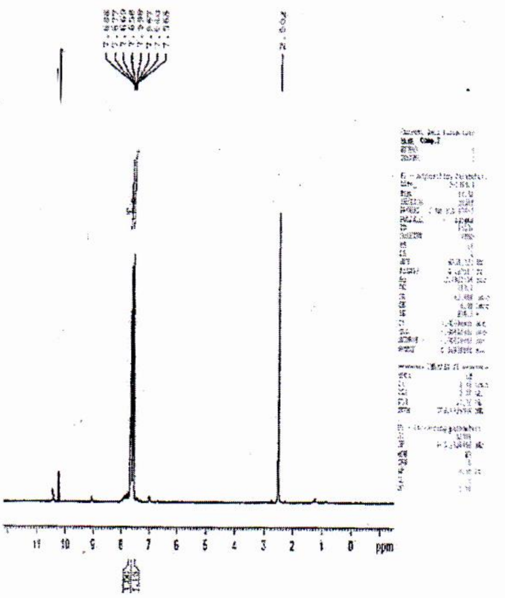


Fig (9) HNMR Spectrum of Compound (3)

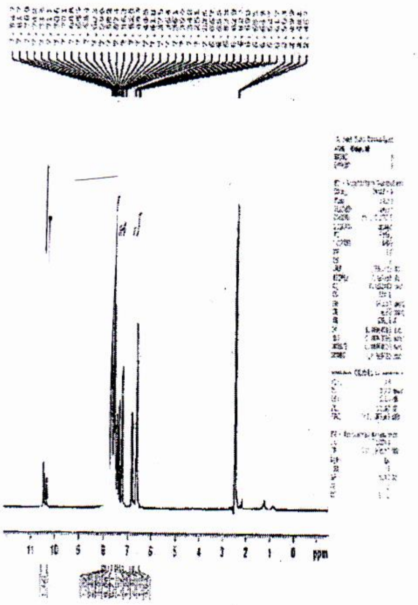


Fig (10) HNMR Spectrum of Compound (5)

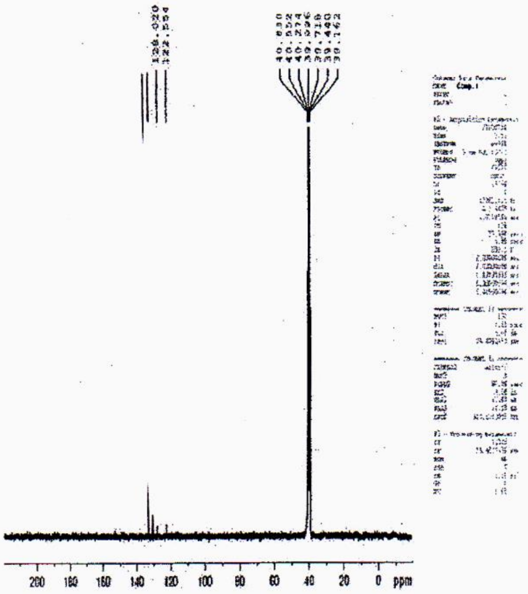


Fig (11) ^{13}CNMR Spectrum of Compound (1)

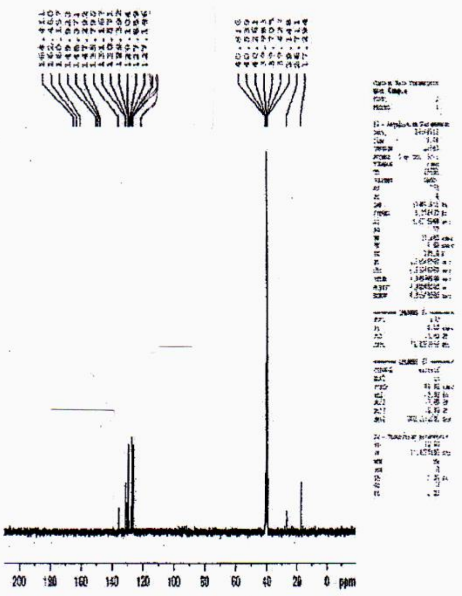


Fig (12) ^{13}CNMR Spectrum of Compound (2)

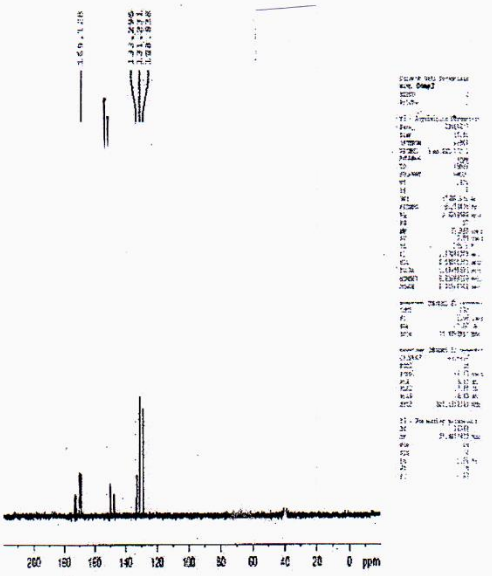


Fig (13) ^{13}CNMR Spectrum of Compound (3)

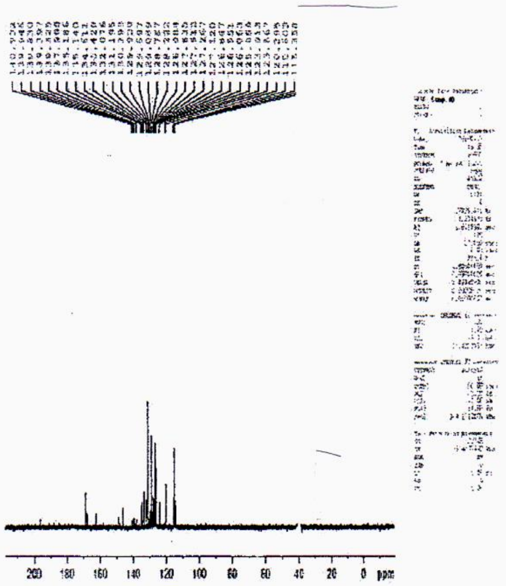
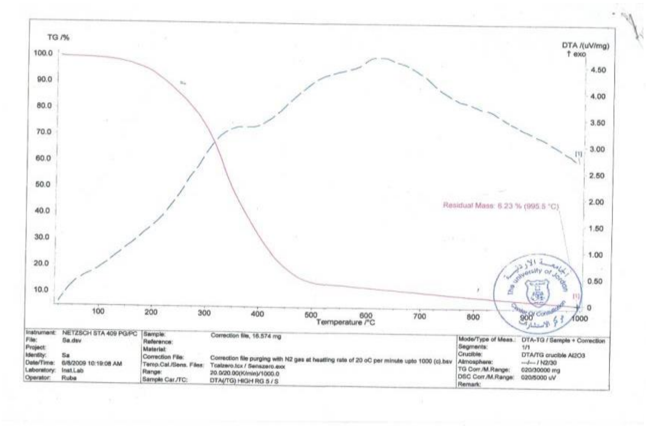


Fig (14) ^{13}CNMR Spectrum of Compound (5)



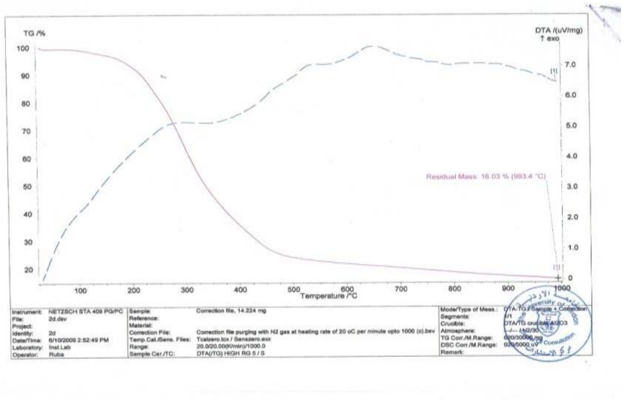
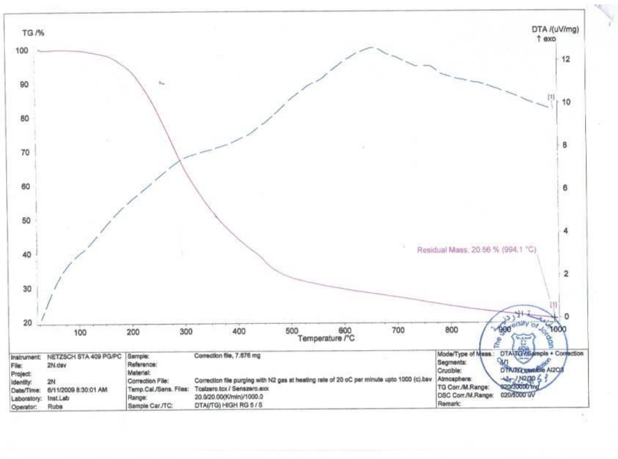


Fig (15) Curing Thermogram of Compound (4)

Fig (16) Curing Thermogram of Compound (5)



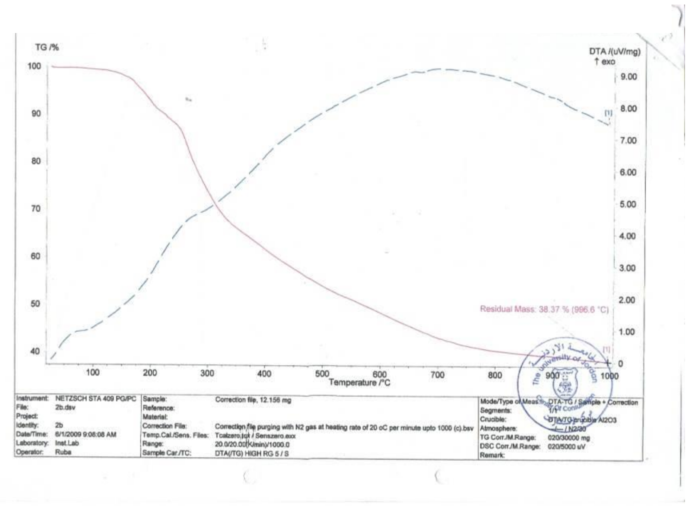
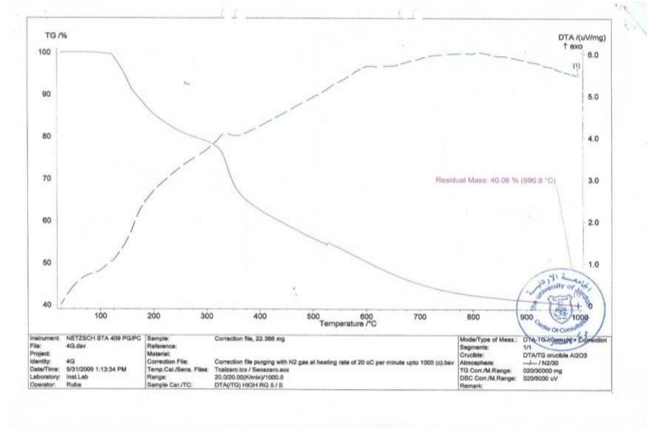


Fig (17) Curing Thermogram of Compound (6)

Fig (18) Curing Thermogram of Compound (8)



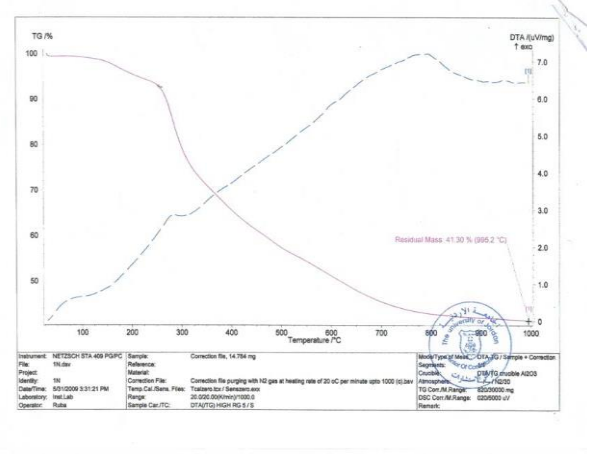


Fig (19) Curing Thermogram of Compound (9)

Fig (20) Curing Thermogram of Compound (10)

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تحضيروتشخيص مشتقات قواعد شيف الفينولية ابتداءا من التيرفثالديهايد

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الخلاصة :

تم تحضير مجموعة من الراتنجات لقواعد شيف الفينولية ابتداءا من المركب الاساسي (التييرفثالديهايد). شخصت جميع المركبات المحضرة باستخدام تقانة مطيافية الاشعة تحت الحمراء (FTIR) وطيف الرنين المغناطيسي (^{1}H-NMR) و (^{13}C-NMR) والتحليل الدقيق للعناصر (C.H.N) مع قياس الثبات الحراري باستخدام تقانة التحليل الحراري الوزني (TGA) للبعض منها.