Synthesis and Characterizationof Some New Phenolic Schiff Bases Derivatives

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Abstract:

Starting from bis (4,4'-diamino phenoxy) ethan(1), a variety of phenolicschiff bases (methylolic, etheric, epoxy) derivatives have been synthesized. All proposed structure were supported by FTIR, ^{1}H-NMR, ^{13}C-NMR Elemental analysis, some derivatives evaluated by thermal analysis (TGA).

Keywords: phenoxy ethane, phenolic schiff bases.

Introduction:

The development of simple Synthetic routes to widely used organic compound using readily available reagents is one of the main objectives of organic Synthesis. The use of Schiff bases covered a wide area applications, in industry and biological field[1]. In industry (phenolic, methylolic, epoxy) Schiff bases were used as a rubber accelerators[2], antioxidants[3] and corrosion inhibitors[2]. They have wide industrial applications as photostabilizers for polyethylene. In analytical chemistry Schiff bases were used for uptake of metal ions[4], and the methylolic resins of some phenolic Schiff bases are used in the accurate determination of trace elements in dilute solution, which is often hindered due to the sensitivity limits of the equipment used for the purpose[5], in this study number of methylolic, etheric and epoxy Schiff bases[6] were prepared from condensation reaction of aromatic aldehyde with [bis(4,4- diaminophenoxy) ethane], the methylolic, etheric and epoxy resins were prepared through condensation with formaldehyde, alcohol, eipychlorohydrine and piperdine, respectively.

Materiala 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, $^{1}H-NMR$, $^{13}C-NMR$ spectra were recorded at 200.13-50.32 MH_z , respectively using tetra methyl Silane (TMS) as an internal standard, (DMSO as a solvent. Elemental analysis were run using a perkin-Elmer RE 2400 (C.H.N) analyzer, thermal stability TGA.

All analysis were performed in center of consultation/ University of Jordan.

Materials

All the chemical used were supplied by (Merk, Fluka and BDH) chemicals, the solvents purified by distillation and dried 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 elute and iodine chamber for spot location.

Thermal graviemetric Analysis (TGA)

Curing of the prepared Schiff bases resins were evaluated by using (thermogravimetric analysis TGA using (NETZSCHESTA/409-PG/PC. Mode/ Type of Meas (DTA-TG).

The programmed heating rate of 20oC/ min from (25-1000) oC under inter atmosphere (N2 gas). So that heat lost or absorbed were recorded fig (15-18) and analyzed table (4).

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Synthesis Bis (4,4'- diamino phenoxy) ethane (1) [7] **:**

Alcoholic sodium hydroxide (0.2mol, 8gm) in 20m/abs. ethanol with (0.02mol, 2.91gm) (p-hydroxy aniline).

To mix admixture until all the solid dissolved, then solve with (0.01mol, 0.64ml) (dibromo ethane). Refluxing 3h, the solute to a pour for groats ice, the solute to come into Being, filtered and recrystallized in ethanol (m.p 238 – 240 ^{o} C) solid, violet.

Synthesis of phenolic Schiff base(2) [6]**:**

Phenolic Schiff base [2] were prepared by well established procedure in the literature[8], condensing (0.02mol, 4.9gm) compound (1) with (0.04mol, 4.9gm) p-hyroxy benzaldehyde, the purity of the products were investigated by T.L.C (m.p 212 – 214 ^{o} C) solid, red..

Synthesis of methylolic phenolic Schiff base resin (3) [8] **:**

A250ml necks round bottomed flask equipped wih mechanical stirrer, condenser and thermometer, the flask was immersed in water bath, then charged with (0.05mol) of phenolic schiff base [2] and (0.05mol, 1.5ml) formaldehyde solution (41-37)%. in 50ml (THF) tetra hydrofuran, the reactants were then mixed gently with ethanolic sodium hydroxide solution (10%) was added portion wise to kept the PH of the reaction mixture (9-10), then heated the mixture in oil bath (50-60) ^{o} C for 3h, the reaction mixture was cooled (5-10) ^{o} C and neutralized with alcoholic phosphoric acid (10%) solution. Organic layer was separated and purified by dissolving in (THF), then filtered to get rid of salt, the product solution was dried using molecular sieves, the solvent was distilled of by rotory evapourator, and the final product was dried in vacuum oven for 24h at 40 ^{o} C.

Synthesis of etheric methylolic Schiff base (4-6) [9] **:**

To mix an appropriate alcohol (CH_3OH , C_3H_7OH, C_4H_9OH) respectively (0.08mol) with (1ml) concentration (H_2SO_4) at groats ice (0-2) ^{o} C, an appropriate methylolic Schiff base [3] (0.4mol) which added gently to the mixture about 1h, Refluxing and increased the temperature gradually to the boiling point of alcohol used, the mixture were kept at boiling alcohol for 24h, then neutralized the cooled mixture by using Sodium hydroxide. The resins formed was extracted using chloroform ($CHCl_3$), dried and evaporated under vacuum, purity by T.L.C.

Synthesis of epoxy phenolic Schiff base (7-10) [10,11] :

To a mixture of an appropriate (0.01mol) phenolic Schiff bases [4-6] with (0.12mol) (eipychlorohydrine) at ice water (0-5) ^{o} C for (15min), then gently added (0.14mol) alcoholic sodium hydroxide in two portions with kept the temperature below (60-65) ^{o} C. The stirring continued for 2h, after first addition the aqueous layer was separated from the organic layer, the second portion of $NaOH$ solution and stirred further for 1h, then left the mixture at the same temperature for (50min), and also the aqueous was separated.

The organic layer was dried and excess of (eipychlorohydrine) and solvent distilled off under reduced pressure. The formed resins were purification by T.L.C.

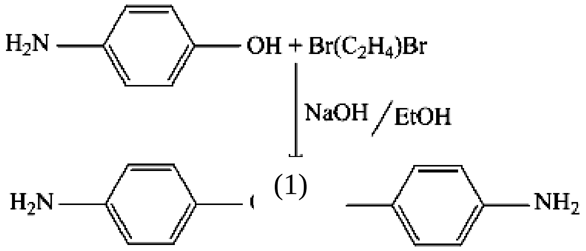
Synthese schiff bases resins with unstitched ring (11-14) [11] :

A mixture of (0.01mol) epoxy [7-10] in (30ml) (1-2) ^{o}C Cold methanol with (0.015mol) piperdine. Refluxing in oil bath (80-100) ^{o}C for (72h), after cooling the solvent evapourated and purification by T.L.C.

All these synthesis steps were summarized in schemes (1-6), physical properties, FTIR, ($^1H, {}^{13}C-NMR$) , elemental analysis, thermal stability (TGA) are listed in tables (1-5), respectively, some compounds evaluated clearly show the temperature rate belong different type dissociation were recorded fig (1-4).

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 [bis (4,4'-diaminophenoxy) ethane](1)

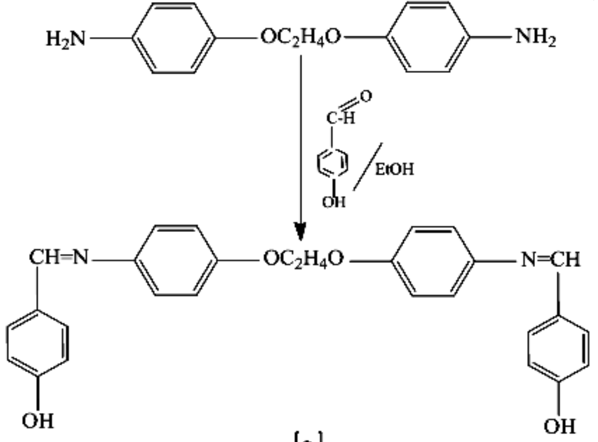


[1]

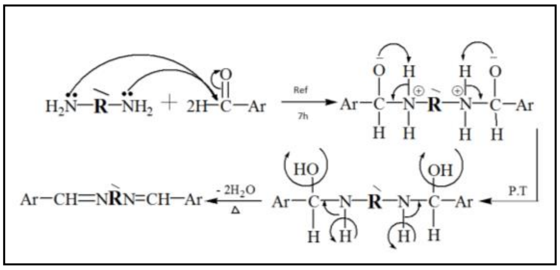
Scheme -1-

The FTIR spectrum [13,14] showed the strong stretching vibration (3420-3375)cm-1 due to (NH_2) groups, (2930-2860) cm-1 for (CH_2) , (1260-1045) cm-1 for (c-o-c), (830) cm-1 for (1,4-disubst), (3080) cm-1 for (Ar-H), (1420) cm-1; for (C-N); 1H-NMR (DMSO-d6) δ: (7.4-7.6)ppm due to (Ar-H), (8.5-6.2)ppm due to (2H,NH2), (1.42-2.81)ppm for (2H,CH2); 13C-NMR(DMSO-d6) δ: (72.4-72.8)ppm for (C-0-C), (128.2-129.3)ppm due to (aromaticcarbons), (143.1-144.6)ppm for (Ar-NH2). Elemental analysis (C.H.N) for compound (1) were fitted according to the (table 3) .

Therefore schiff base (2) prepared by the condensation of the corresponding compound (1) with (p-hydroxybenzaldehyde in refluxing



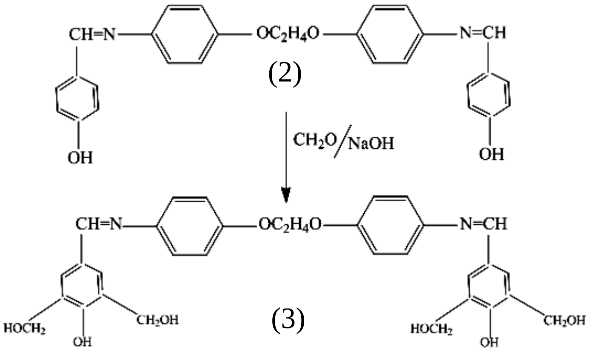
[2]

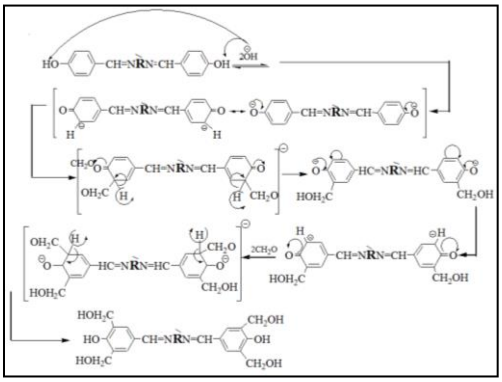


(2)

Scheme -2-

The reaction proceeds by the nucliophilic attach of the nucleophilic nitrogen atom of the amine on the carbonyl group of aldehyde with the loss of water molecular to give a stable compound in good yield, the FTIR spectrum showed the strong bands (1602)cm-1 for (C=N) combined with disappearance of stretching bands (3420-3325) cm-1 of (NH2), strong bands (3400-3240) cm-1 for (OH) and (1150-1160) cm-1 absorption bands for phenolic group (C-O); 1H-NMR (DMSO-d6) δ: (7.73-7.85)ppm for (Ar-H), (10.12-10.16)ppm (H,OH); 13C-NMR (DMSO-d6) δ: (128.2-128.9)ppm (caromatic carbons), (115.2-117.2)ppm for (C,=CH), (148.5-152.6)ppm for (C=N), (155.1-156.0)ppm for (Ar-OH).Elemental analysis for compound (2) were fitted according to the (table 3) .Refluxing compound (2) with formaldehyde afforded methylolic resins (3) which consisting of hydroxyl methylene group (-CH2OH) known as a methylol groups which are chemically very reactive functional groups:

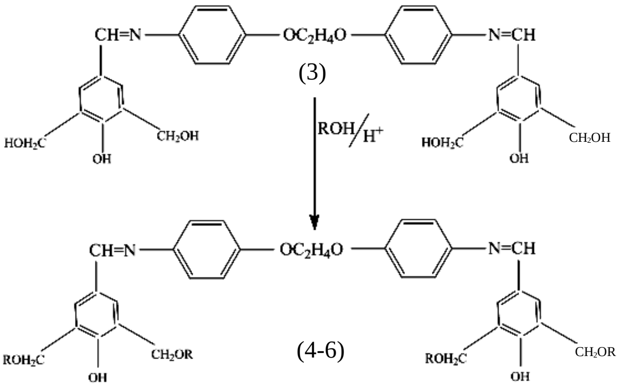




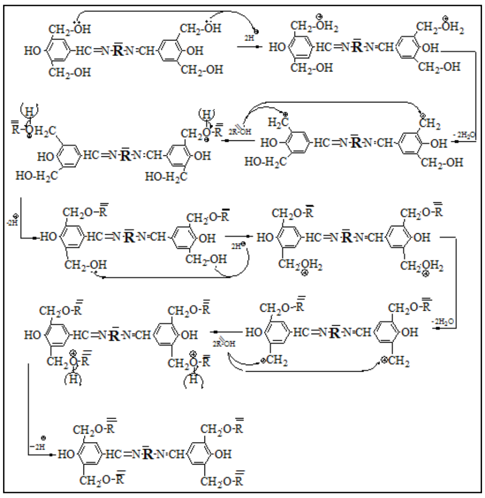
Scheme -3-

Compound (3) indicated by (FTIR) spectrum of abroad stretching bands at (3417-3265)cm-1 for methylolic groups combined with strong stretching bands at (2954-2896)cm-1 for aliphatic (CH2) ; 1H-NMR(DMSO-d6) δ:(7.20-8.10)ppm due to (Ar-H), (10.62-10.89) ppm for (H,OH), (1.06-2.90)ppm for (t,2H,CH2); 13C-NMR(DMSO) δ: (126.5-126.8)ppm (aromatic carbons), (120-124)ppm for (C,=CH), (154.8-154.9)ppm for (Ar-OH). Emental analysis for compound (3) were fitted according to the (table 3) .

Compound (3) similarly reacts with (methanol propanol, Butanol) afforded etheric resins (4-6):

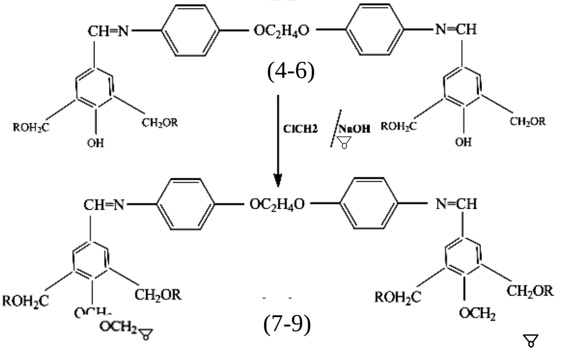


R = -CH3 , -C3H7 , - C4H9

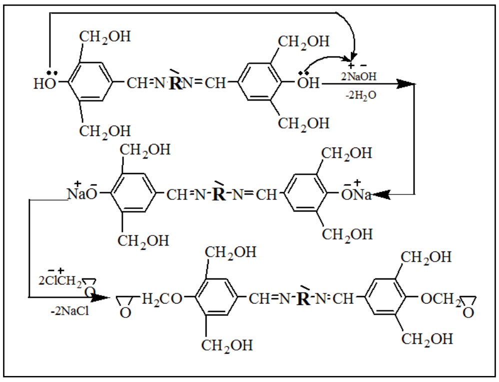


Scheme -4-

Compound [4] indicated in FTIR spectrum of stretching vibration is more sharp bands at (2980-2975)cm-1 for (CH2) and strong vibration at (1226-1168) cm-1 for (C-O-C); 1H-NMR(DMSO-d6) δ: (7.3-7.6)ppm due to (Ar-H), (2-2.2)ppm for (3H, CH3), (10.01-10.21)ppm for (H,OH); 13C-NMR(DMSO-d6) δ: ((11.5-116.4)ppm due to (aromatic carbons), (149-151)ppm due to (C=N), (154.2-154.9)ppm due to (Ar-OH), 972.1-72.6)ppm for (C-O-C). Elemental analysis for compound [4] were fitted according to the (table 3) .Similarly react compounds (4-6) with eipychlorohydrine afforded (7-9) derivatives respectively.

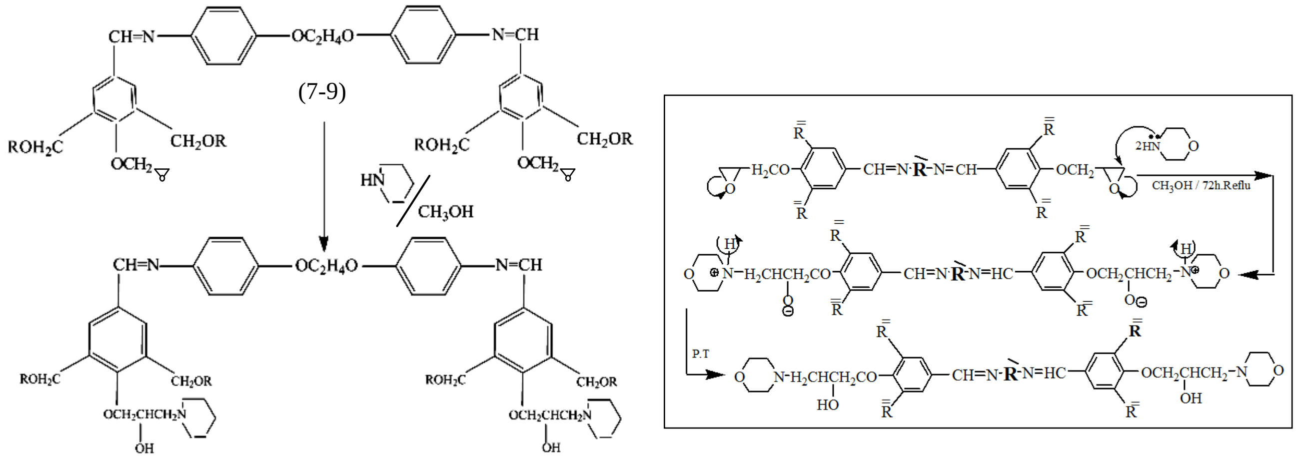


R = -CH3 , -C3H7 , - C4H9



Scheme -5-

Compound (7) obtained FTIR spectrum for sharp bands for oxarine absorption at (948-995) cm-1 and strong bands (2931-2873) cm-1 for (CH2), (1130-1090) cm-1 for (C-O-C); 1H-NMR(DMSO-d6) δ: (7.2-7.5)ppm for (Ar-H), (1.9-2.1)ppm due to (3H, CH3); 13C-NMR (DMSO-d6) δ: (129.3-130.1)ppm . (aromatic carbons), (2.1-2.3)ppm for (CH2, oxarine), (72.6-72.9)ppm due to (C-O-C). Elemental analysis for compounds (7) were fitted according to the (table 3) . Finally (7-9) compounds react with piperdine a corresponding (10-12) respectively



(10-12)

R = -CH3 , -C3H7 , - C4H9

Scheme -6-

The FTIR spectrum of compound (10) obtained increasing in stretching vibration of (OH) at (3479-3437) cm-1 and (1220-1225) cm-1 for (C-O), (1268-1238) cm-1 due to (C-O-C); 1H-NMR(DMSO-d6) δ: (7.8-7.9)ppm due to (Ar-H), (9.7-9.8) due to (H,OH), (1.39-1.41)ppm for (2H,CH2); 13C-NMR(DMSO-d6) δ: (72.8-72.9)ppm due (C-O-C), (129.3-130.1)ppm for (aromatic carbons). Elemental analysis for compounds [10] were fitted according to the (table 3) .All these steps were summarized in schemes (1-6) physical properties of all mentioned and other details [FTIR, Elemental analysis, TGA, analysis, 1H-NMR, 13C-NMR,] , data are listed in tables (1-5) respectively, curing thermal stability of some compounds were evaluated by using (TGA) table (4) is clearly show the temperature rate belong to different type dissociated for derivatives, fig(15-18) .

Table (1) Dapcited physical properties for (1-12) compounds

No	Molecular formula	M.P Co	Colour	Yield %	Purification solvent	Comp No	Molecular formula	M-P Co	Colour	Yield %	Purification solvent
1	C14H16N2O2	238-240	Pale violate	90	Ethanol	7	C42H42N2O10	Oily	Brown	60	THF
2	C28H24N2O4	212-214	Deep Red	87	Ethanol	8	C42H54N2O10	Oily	Brown	65	THF
3	C32H32N2O8	Oily	Brown	80	THF	9	C54H72N2O10	Oily	Brown	60	THF
4	C36H40N2O8	Oily	Brown	75	THF	10	C52H66N4O10	Oily	Brown	70	Methanol
5	C44H56N2O8	Oily	Brown	75	THF	11	C60H86N2O10	Oily	Brown	72	Methanol
6	C48H64N2O8	Oily	Brown	65	THF	12	C64H94N2O10	Oily	Brown	65	Methanol

Table (2) FTIR spectral data of (1-12)

No	VOH	VCH2	VC-O-C	VC-O	Others	No	VOH	VCH2	VC-O-C	VC-O	Others
1	-	2930 2860	1260 1045	-	VNH2(3420-3325) VC-N(1420)	7	3257 3225	2931 2873	1201 1205	1110 1045	 (948-995)
2	3400 3240	2910 2850	1200 1212	1228 1200	VC=N(1602) VC=C(1597)	8	3290 3155	2910 2875	1240 1210	1202 1120	 (917-892)
3	3417 3265	2954 2896	1192 1100	1245 1227	VC=N(1612) V=CH(3080)	9	3100 3280	2935 2870	1235 1228	1213 1108	 (914-910)
4	3200 3245	2980 2975	1226 1168	1197 1160	VC=N(1608) V=CH(3100)	10	3479 3437	2900 2865	1268 1238	1220 1225	VC-N(1220)
5	3285 3260	2985 2980	1218 1210	1100 1097	VC=N(1615) V=CH(3009)	11	3310 3260	2910 2845	1250 1255	1200 1195	VC-N(1238)
6	3290 3270	2972 2968	1220 1214	1113 1085	VC=N(1612) V=CH(3116)	12	3316 3280	2900 2886	1260 1265	1196 1190	VC-N(1244)

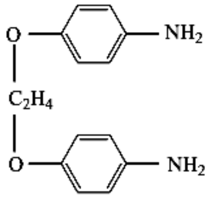
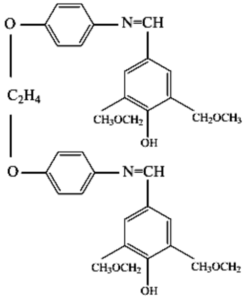
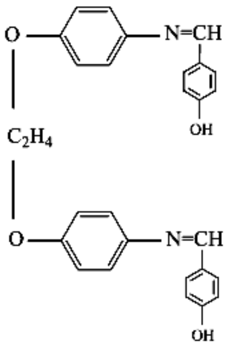
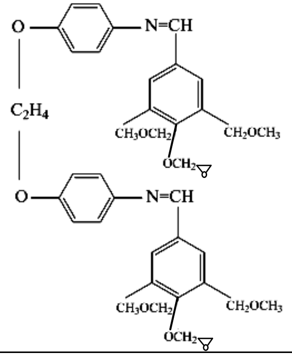
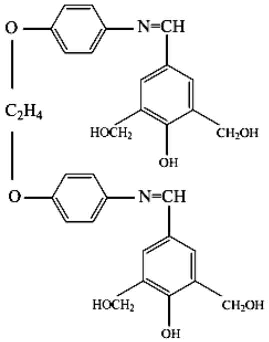
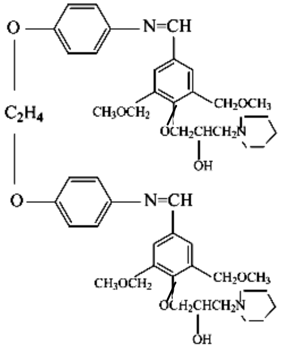
Table (3) Depacited Elemental analysis (C.H.N) for some compounds.

No.	(C.H.N) analysis calculated (found)			Comp No.	(C.H.N) analysis calculated (found)		
1	68.89 (69.20)	6.56 (7.53)	11.48 (12.68)	4	72.48 (73.39)	6.71 (7.90)	4.70 (5.69)
2	74.34 (75.41)	5.31 (6.30)	6.20 (6.98)	7	68.67 (69.93)	5.72 (6.91)	3.82 (4.91)
3	67.13 (68.20)	5.59 (6.60)	4.90 (5.95)	10	68.87 (69.86)	7.29 (8.28)	6.18 (7.18)

Table (4) Show the Curing temperature of some Compounds

Comp No	Primary dissociated	Finally dissociated	50% dissociated	Maximum dissociated	Average dissociated	% Char content
3	220	380	350	310	0.25	93.77
4	225	400	300	280	0.128	92.73
7	180	750	612	325	0.069	61.63
10	165 260	700	660	360	0.053	58.70

Table (5) 1H-NMR and 13C-NMR spectral data for some compounds.

No	Compound Structure	1H-NMR/ data	13C-NMR/ data	No	Compound Structure	1H-NMR/ data	13C-NMR/ data
1		δ: 74-7.6 (Ar-H) δ: 8.5-6.2(2H, NH2) δ: 1.42-2.81(2H, CH2)	δ: 72.4-72.8(C-O-C) δ: 128.2-129.3(aromatic carbons). δ: 143.1-144.6(Ar-NH2)	4		δ: 7.3-7.6(Ar-H) δ: 2-2.1(3H,CH3) δ: 10.01-10.21(H,OH)	δ: 115.2-116.2(aromatic carbons). δ: 149-151(C=N) δ: 154.2-154.9(Ar-OH) δ: 72.1-72.6(C-O-C)
2		δ: 7.73-7.85(Ar-H) δ: 10.12-10.16(H,OH)	δ: 128.2-128.9(aromatic carbons). δ: 115.2-117.2(C,=CH) δ: 148.5-152.6(C=N) δ: 155.1-156(Ar-OH)	7		δ: 7.2-7.5(Ar-H) δ: 1.9-2.1(3H,CH3)	δ: 129.3-130.1(aromatic carbons). δ: 2.1-2.3(CH2,oxarine) δ: 72.6-72.9(C-O-C)
3		δ: 7.20-8.10(Ar-H) δ: 10.62-10.89(H,OH) δ: 1.06-2.90(t,2H,CH2)	δ: 126.5-126.3(aromatic carbons). δ: 120-124(C,=CH) δ: 154.8-154.9(Ar-OH)	10		δ: 7.8-7.9(Ar-H) δ: 9.7-9.8(H,OH) δ: 1.39-1.41(2H,CH2)	δ: 72.8-72.9(C-O-C) δ: 129.3-130.1(aromatic carbons).

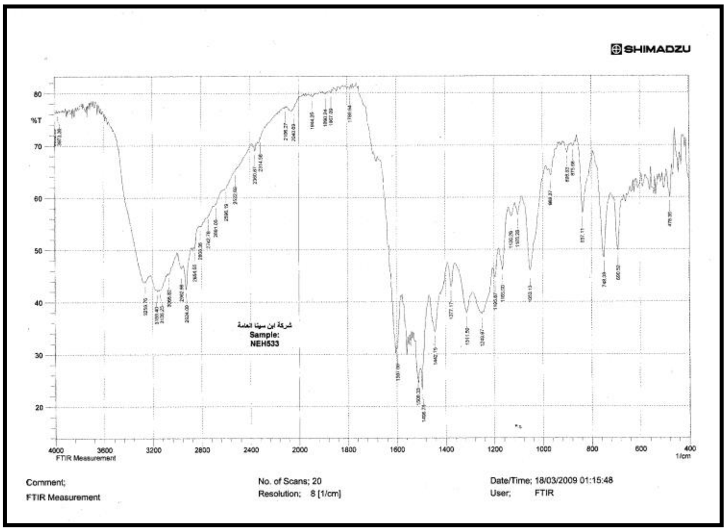


Fig. (1) FT-IR for compound (1)

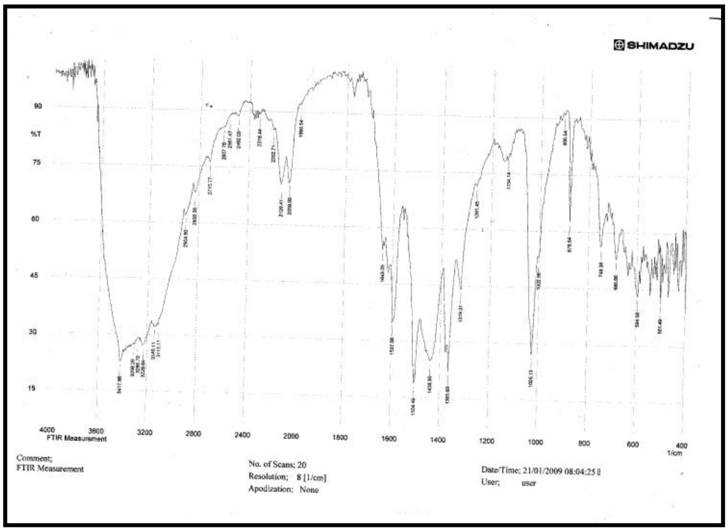


Fig. (2) FT-IR for compound (2)

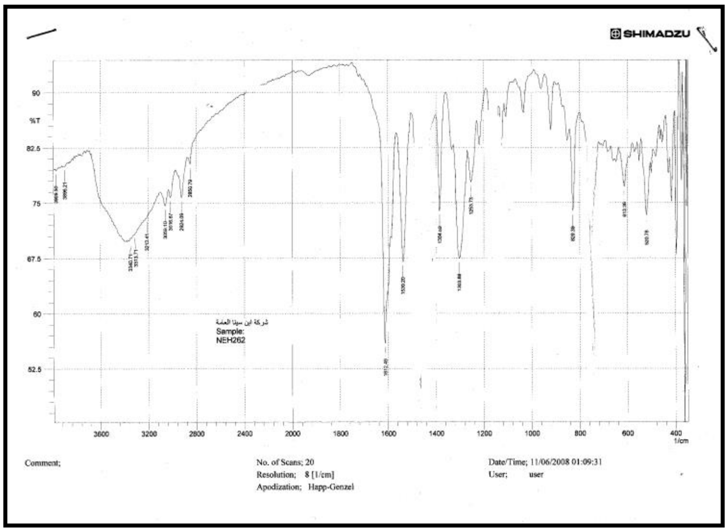


Fig. (3) FT-IR for compound (3)

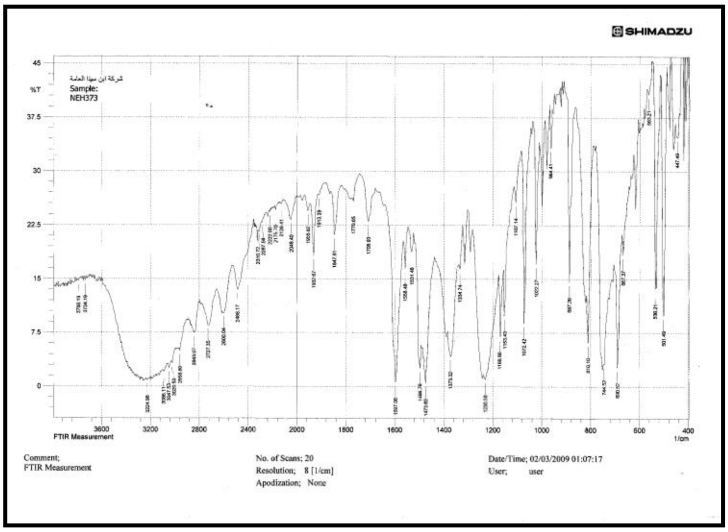


Fig. (4) FT-IR for compound (4)

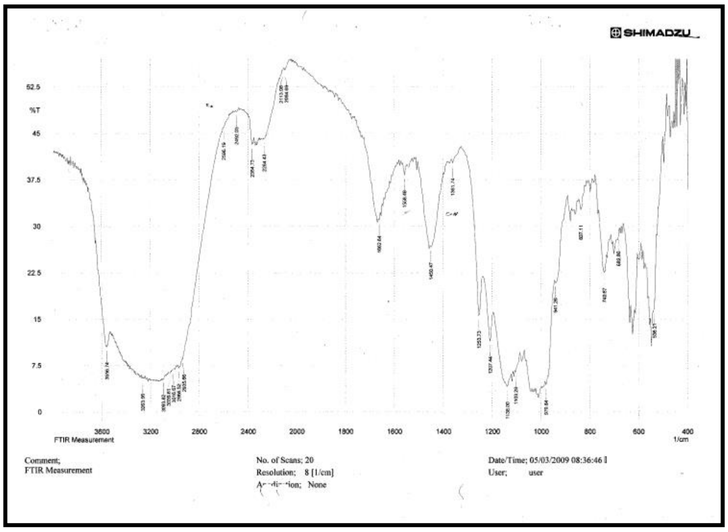


Fig. (5) FT-IR for compound (7)

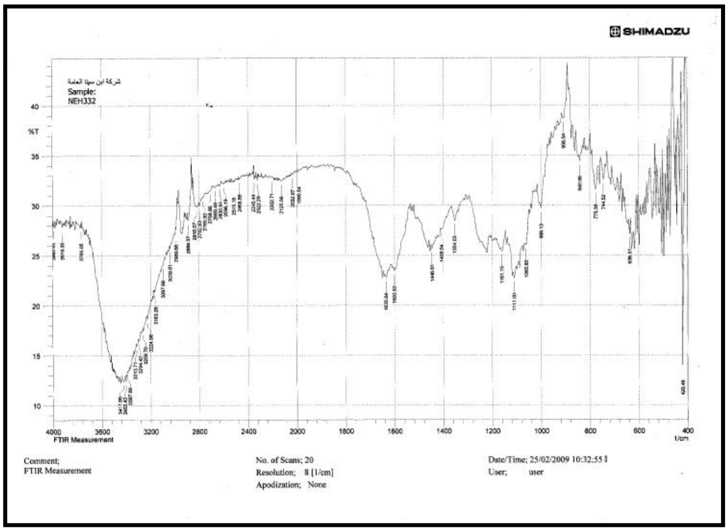


Fig. (6) FT-IR for compound (10)

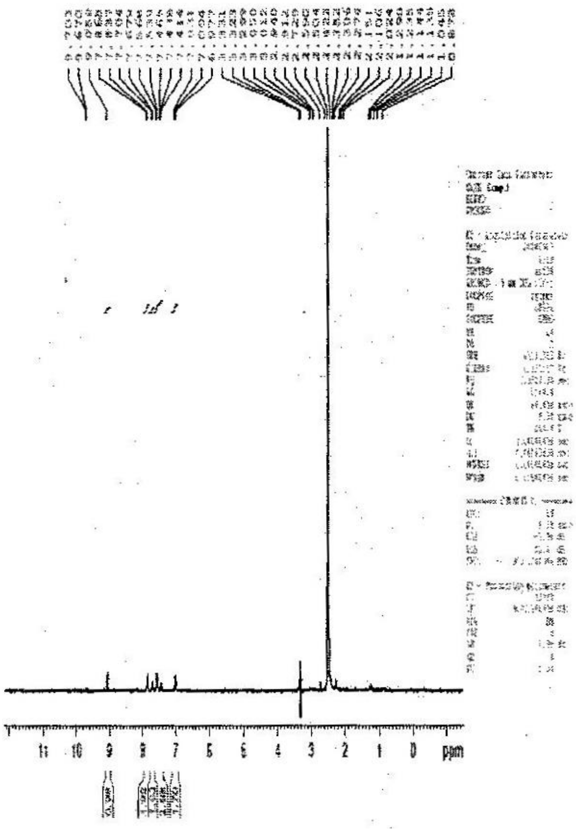


Fig. (7) HNMR Spectrum of Compound (1)

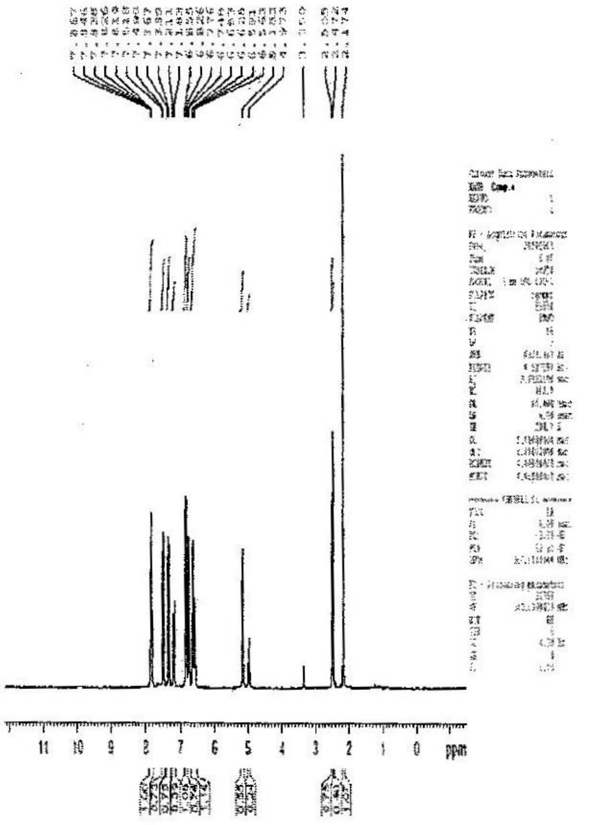


Fig. (8) HNMR Spectrum of Compound (4)

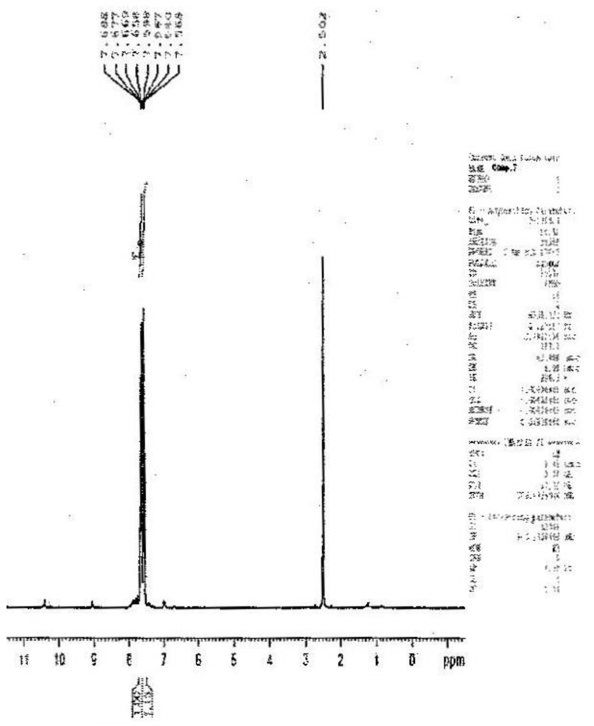


Fig. (9) HNMR Spectrum of Compound (7)

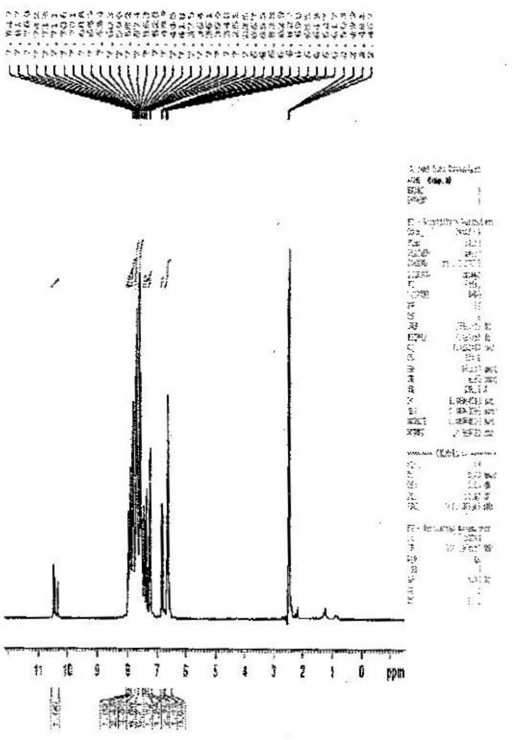


Fig. (10) HNMR Spectrum of Compound (10)

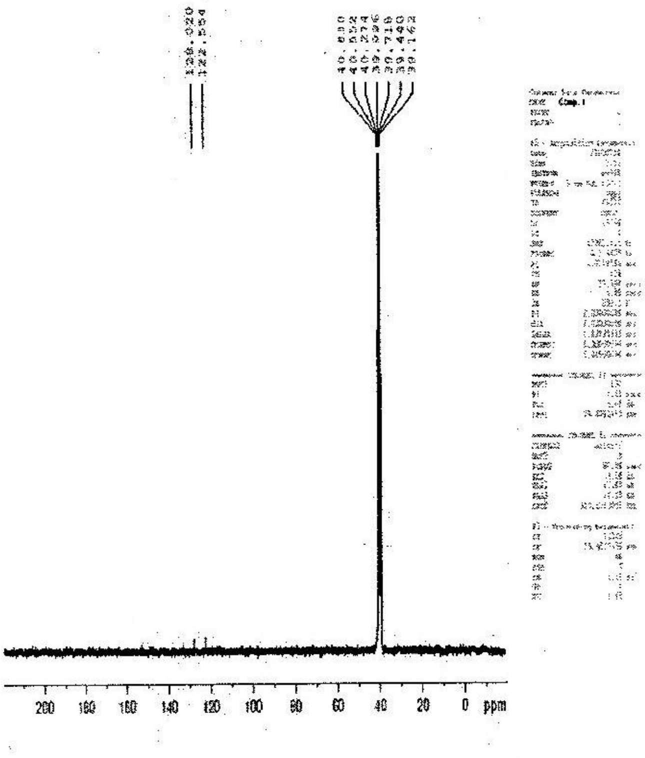


Fig. (11) ^{13}CNMR Spectrum of Compound (1)

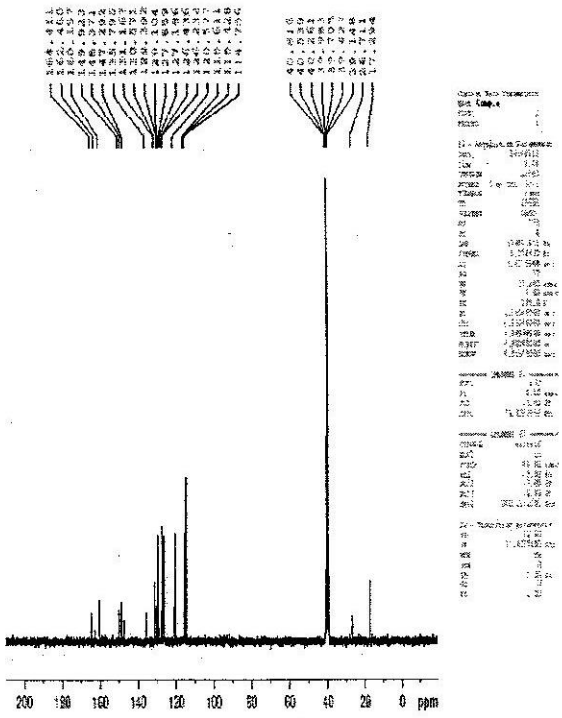


Fig. (12) ^{13}CNMR Spectrum of Compound (4)

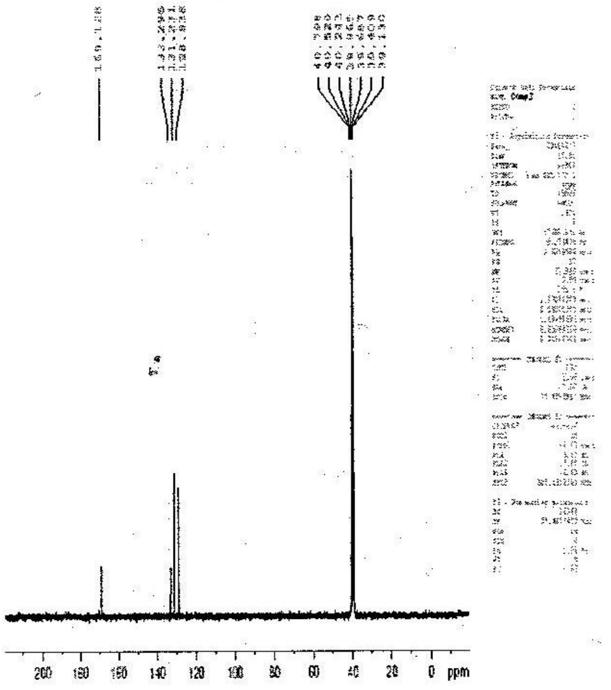


Fig. (13) ^{13}CNMR Spectrum of Compound (7)

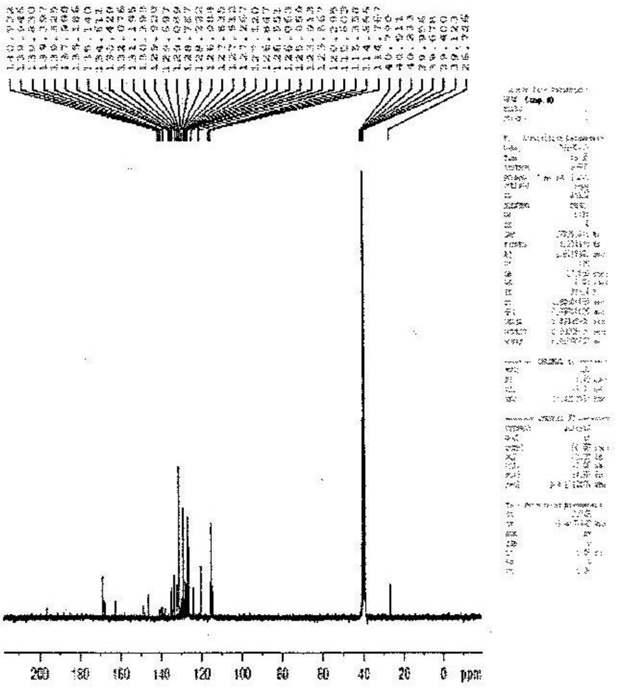


Fig. (14) ^{13}CNMR Spectrum of Compound (10)

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تحضير وتشخيص بعض مشتقا ت قواعد شيف الفينولية

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الخلاصة:

ابتداءا من المركب (4 و$4^{/}$ ثنائي امين فينوكسي) ايثان(1)، حضرت عدد من مشتقات قواعد شيف الفينولية (الميثيلولية، الايثرية، الايبوكسية).........

لقد تم تشخيص المركبات الجديدة بمطيافية الاشعة تحت الحمراء وطيف الرنين المغناطيسي (1H,13C-NMR) والتحليل الكمي الدقيق للعناصر (C.H.N) مع قياس آلية الثبات الحراري باستعمال تقنية التحليل الحراري الوزني TGA .