

Synthesis and Characterization of Derivatives Based on 4,4'-Dimercaptobiphenyl

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Abstract:

Starting from 4,4'-Dimercaptobiphenyl, a variety of phenolic Schiff bases (methylolic, etheric, epoxy) derivatives have been synthesized. All proposed structure were supported by FTIR, ¹H-NMR, ¹³C-NMR Elemental analysis all analysis were performed in center of consultation in Jordan Universty.

Keywords: dimercaptobiphenyl, phenolicschiff bases.

Introduction:

The development of simple Synthetic routes too 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], atorsantioxidants[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 (4,4'-Dimercaptobiphenyl)[7]

Materials And Methods:

Melting points were determined on Gallenkamp, melting point apparatus and were uncorrected. FTIR spectra of

the compounds were recorded on a (SHIMADZU) FTIR. 8300 Spectrometer as KBR-disc, spectra were recorded at 200.13-50.32, respectively using tetra methyl Silane (TMS) as internal standard, (DMSO as solvent. Elemental analysis were run using a perkin-Elmer RE 2400 (C.H.N) analyzer. All analysis were performed in center of consultation/ University of Jordan. 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.

Preparation of [4,4'-di-hydrazino biphenyl (1)][7]:

A mixture of (0.01 mol, 2.18gm) [4,4'-Dimercaptobiphenyl] with (0.02mol, 0.64ml) hydrazine hydrate (99%) in (10ml) ab. ethanol. Refluxing 6h or until ceased H₂S, then cooled the mixture, filtered and crystallized in ethanol.

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

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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-hydroxybenzaldehyde, the purity of the products were investigated by T.L.C.

Synthesis of methylolic phenolic Schiff bases resin (3)[8]

A250ml necks round bottomed flask equipped with 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 the mixture was heated in oil bath (50-60)^oC for 3h, the reaction mixture was cooled (5-10)^oC and neutralized with alcoholic phosphoric acid (10%) solution. Organic layer was separated and purified by dissolving in (THF), then filtered to get rid off salt, the product solution was dried using molecular sieves, the solvent was distilled off by rotaryevapourator, and the final product was dried in vacuum oven for 24h at 40^oC.

Synthesis of etheric methylolic Schiff bases (4-5)[9]:

To mixed an appropriate alcohol (0.08mol) with (1ml) concentration () at groats ice (0-2)^oC, an appropriate methylolic Schiff base [3] (0.4mol) which gently added to the mixture about 1h, Refluxing with increasment of the temperature gradually to the boiling point of the alcohol used,then the mixture was kept at boiling alcohol for 24h,and neutralized the cooled mixture by using Sodium hydroxide. The resins formed was extracted using chloroform (), dried and evaporated under vacuum, purified by T.L.C. techniques

Synthesis of epoxy phenolic Schiff bases (6-7)[10-11]:

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

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

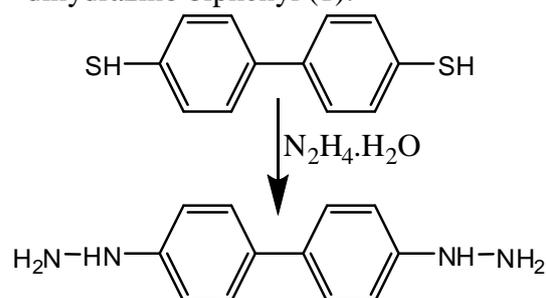
Synthesis schiff bases resins with unstitched ring (8-9)[11]:

A mixture of (0.01mol) epoxy compound [7-10] in (30ml) (1-2)^oC Cold methanol with (0.015mol) morpholine. Refluxing in oil bath (80-100)^oC 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, (), elemental analysis, are listed in tables (1-4), respectively.

Results And Discussion:

Considerable interest have been expressed in synthesis of schiff bases in recent year due to their industrial and biological importance, starting from 4, - dihydrazino biphenyl (1):

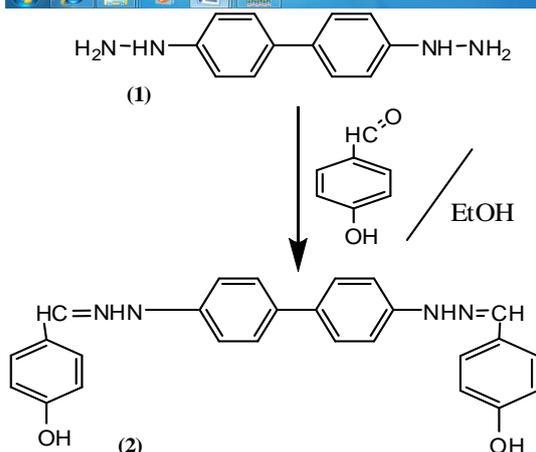
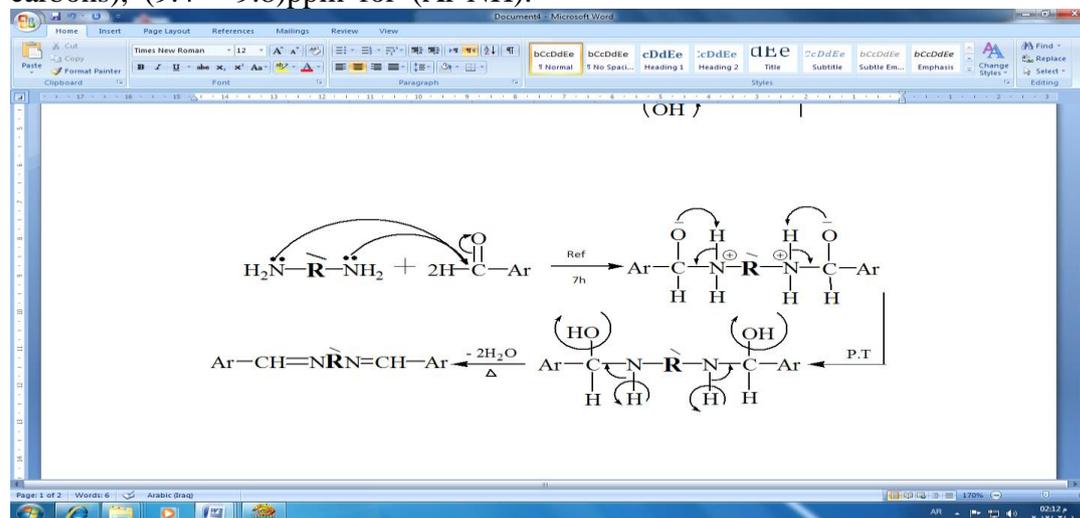


Scheme -1-

The FTIR spectrum [12,13] showed the strong stretching vibration (3420-3210) cm^{-1} due to (1361-1385) cm^{-1} for (830) cm^{-1} for (1,4-disubst), (3080) cm^{-1} for (Ar-H), (1420) cm^{-1} ; for (C-N); $^1\text{H-NMR}$ (DMSO- d_6) δ : (7.4-7.6)ppm due to (Ar-H), (4.1-4.6)ppm due to (4H,NHNH); $^{13}\text{C-NMR}$ (DMSO- d_6) δ : (128.2-129.3)ppm due to (aromatic carbons), (9.4 - 9.8)ppm for (Ar-NH).

Elemental analysis (C.H.N) for compound (1) $\text{C}_{12}\text{H}_{14}\text{N}_4$: [67.29(68.29); H, 6.54(7.50); N, 26.17(27.18)]

There for schiff base (2) prepared through condensation of the corresponding compound (1) with (p-hydroxy benzaldehyde in refluxing ethanol.

**Scheme -2-**

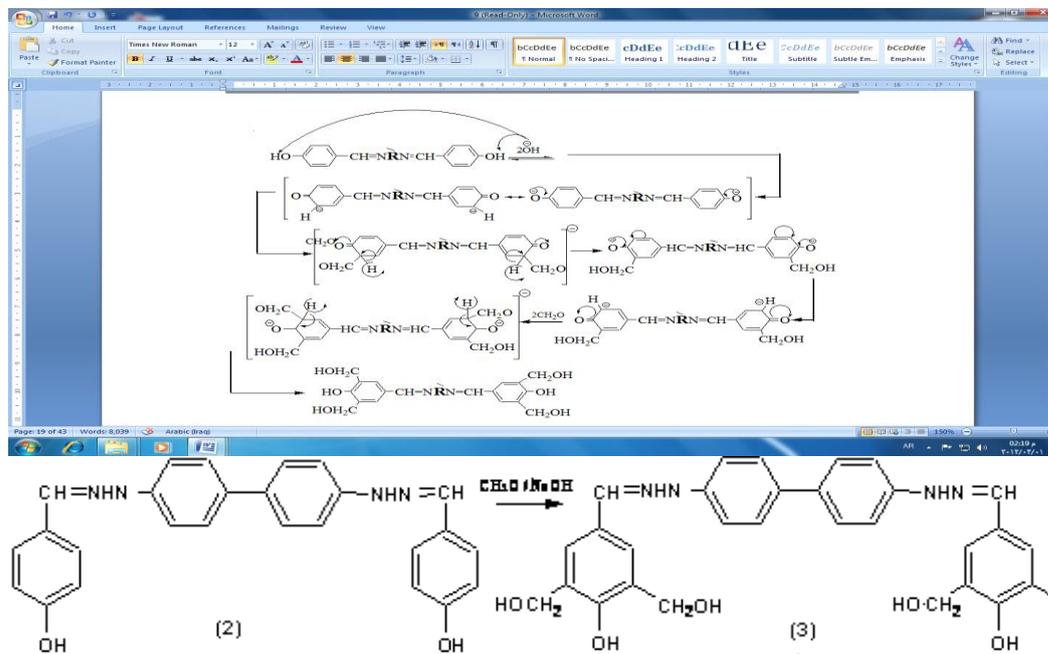
The reaction proceeds by the nucleophilic attack of the nucleophilic nitrogen atom of the amine on the carbonyl group of aldehyde with the loss of water molecular to give a stable compound in good yield, the FTIR spectrum showed the strong bands (1600) cm^{-1} for (C=N) combined with disappearance of stretching bands (3420-3210) cm^{-1} of (NHNH₂), strong

bands (3400-3240) cm^{-1} for (OH) and (1150-1160) cm^{-1} absorption bands for phenolic group (C-O); $^1\text{H-NMR}$ (DMSO- d_6) δ : (7.73-7.85)ppm for (Ar-H), (10.12-10.16)ppm (H,OH); $^{13}\text{C-NMR}$ (DMSO- d_6) δ : (128.2-128.9)ppm (aromatic 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) $C_{26}H_{22}N_4O_2$: [C,73.93(74.93); H, 5.21(6.20); N, 13.27(14.30)].

Refluxing compound (2) with formaldehyde afforded methylolic

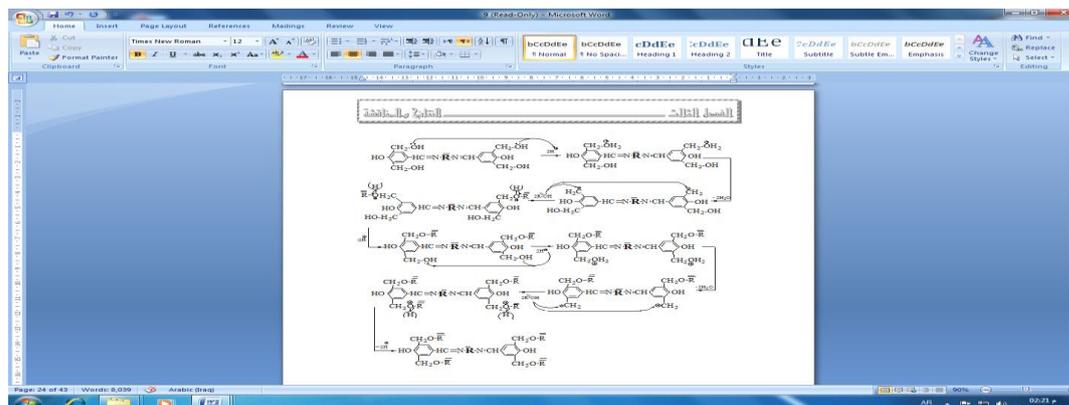
resins (3) which is consisting of hydroxyl methylene group (-CH₂OH) known as methylol groups which are chemically very reactive functional groups:

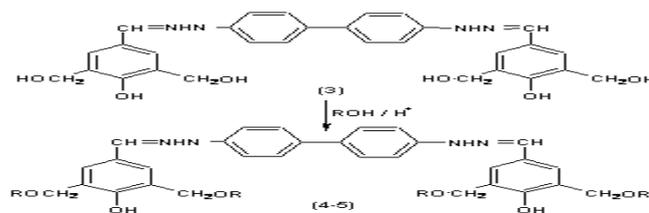


Scheme -3-

Compound (3) indicated by (FTIR) spectrum of abroad stretching bands at $(3465-3292)cm^{-1}$ for methylolic groups combined with strong stretching bands at $(2954-2896)cm^{-1}$ for aliphatic (CH₂) ; ¹H-NMR(DMSO-d₆) δ:(7.7-7.9)ppm due to (Ar-H), (10.3-11.1) ppm for (H,OH), (1.50-2.20)ppm for (t,2H,CH₂);

¹³C-NMR(DMSO) δ: (126.5-126.8)ppm (aromatic carbons), (115.6-115.8)ppm for (C,=CH), (154.8-154.9)ppm for (Ar-OH). Elemental analysis for compound (3) $C_{30}H_{30}N_4O_6$: [C,66.42(67.40); H, 5.54 (6.50); N, 10.33(11.30)]. Compound (3) similarly react with (methanol , propanol) afforded etheric resins (4-5):





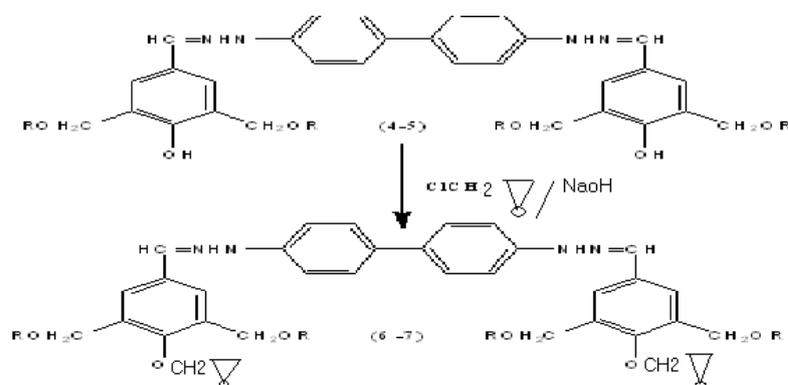
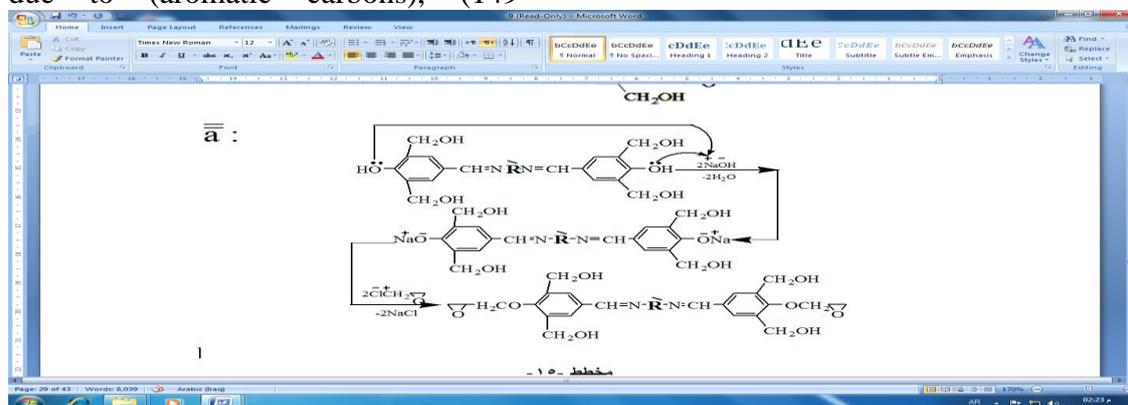
scheme-4-

R= -CH₃, -C₃H₇

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] C₃₄H₃₈N₄O₆: [C, 68.23(69.23); H, 6.35(7.33); N, 9.37(10.30)].

Similarly react compounds (4-5) with eipychlorohydrine afforded (6-7) derivatives respectively.



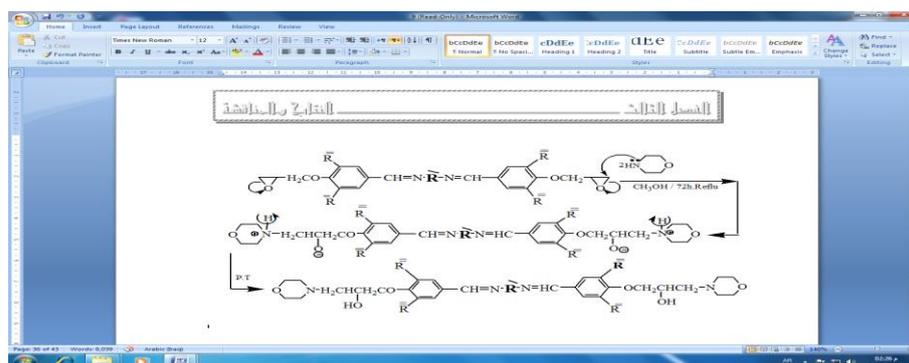
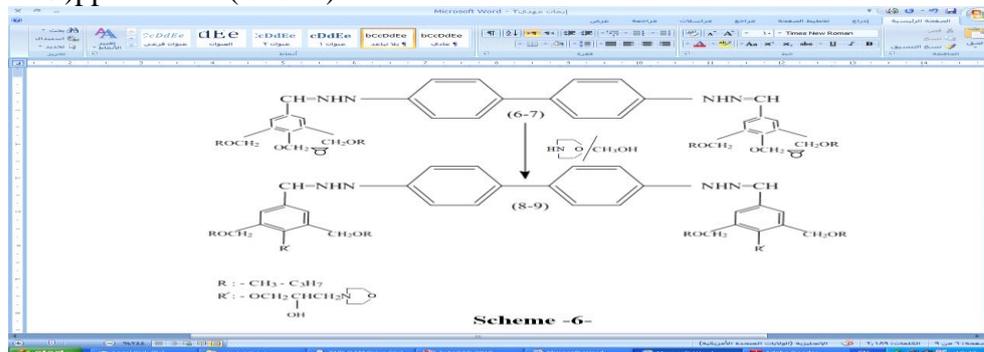
Scheme -5-

Compound (6) 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 (6) C₃₈H₄₂N₄O₈: [C, 66.86(67.80); H, 6.61(7.16); N, 8.21(9.21)]. Finally (6-7) compounds react with morpholine a corresponding (8-9) respectively.



Scheme 6-

The FTIR spectrum of compound (8) 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 [8] C₄₈H₆₂N₆O₁₀:

[C,65.53(66.52); H, 7.03 (8.04); N, 9.52(10.50)].

All these steps were summarized in schemes (1-6) physical properties of all mentioned and other details [FTIR, Elemental analysis, ¹H-NMR, ¹³C-NMR,] , data are listed in tables (1-5) respectively.

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

| No | Molecular formula | M-P C° | Colour | Yield% | Purification solvent | Comp No | Molecular formula | M-P C° | Colour | Yield% | Purification solvent |
|----|---|---------|------------|--------|----------------------|---------|--|--------|--------|--------|----------------------|
| 1 | C ₁₂ H ₁₄ N ₄ | 222-224 | Orange | 87 | Ethanol | 6 | C ₄₂ H ₄₆ N ₄ O ₈ | Oily | Brown | 72 | THF |
| 2 | C ₂₆ H ₂₄ N ₄ O ₂ | 200-902 | Orange | 75 | THF | 7 | C ₄₈ H ₆₂ N ₄ O ₈ | Oily | Brown | 75 | THF |
| 3 | C ₃₀ H ₃₀ N ₄ O ₆ | Oily | Redish | 75 | THF | 8 | C ₄₈ H ₆₄ N ₄ O ₁₀ | Oily | Brown | 70 | Methanol |
| 4 | C ₃₄ H ₃₈ N ₄ O ₆ | Oily | Pale brown | 70 | THF | 9 | C ₅₄ H ₈₀ N ₄ O ₁₀ | Oily | Brown | 70 | Methanol |
| 5 | C ₄₂ H ₅₄ N ₄ O ₆ | Oily | Pale brown | 70 | THF | | | | | | |

Table 2: FTIR spectral data of (1-9) compounds

| Comp No | V _{OH} | V _{CH₂} | V _{C-O-C} | V _{C=N} | V _{C=C} | Others |
|---------|-----------------|-----------------------------|--------------------|------------------|------------------|--|
| 1 | - | - | - | - | 1597 1580 | V _{NHNH₂} (3450-3210) V _{N-N} (1535) |
| 2 | 3400 3300 | - | 1600 | | 1586 | V _{C-o} (1200) V _{C-o} (1145) |
| 3 | 3465 3292 | 2954 2896 | 1612 | | 1575 | V _{C-o} (1196) |
| 4 | 3400 3255 | 2980 2975 | 1620 | | 1570 | V _{C-o} (1190) |
| 5 | 3380 3250 | 2960 2889 | 1620 | | 1560 | V _{C-o} (1200) |
| 6 | 3310 3250 | 2931 2873 | 1616 | | 1570 | (948-995) |
| 7 | 3300 3270 | 2960 2940 | 1610 | | 1591 | (932-985) |
| 8 | 3479 3437 | 2970 2975 | 1618 | | 1585 | V _{C-o} (1220) V _{C-o} (1225) |
| 9 | 3450 3421 | 2950 2945 | 1620 | | 1587 | V _{C-o} (1218) V _{C-o} (121) |

Table 3: ¹H-NMR and ¹³C-NMR spectral data for some compounds

| No | Compound Structure | ¹ H-NMR/ data | ¹³ C-NMR/ data | No | Compound Structure | ¹ H-NMR/ data | ¹³ C-NMR/ data |
|----|--------------------|---|--|----|--------------------|---|--|
| 1 | | δ : (7.2-7.8) (Ar-H) δ : (4.1-4.6)(d,4H, NHNH) | δ : (130.2-131.2) (aromatic carbons). δ : (9.4-9.8) (Ar-H). δ : (115.1-115.3) (C=CH). | 4 | | δ : (7.9-8.2)(Ar-H) δ : (2.3-2.5)(3H,CH ₃) δ : (10.8-11.2)(H,OH) | δ : (115.8-117) (aromatic carbons). δ : (149-152) (C=N) δ : (154.2-155.3) (Ar-OH) δ : (72-73) (C-O-C) |

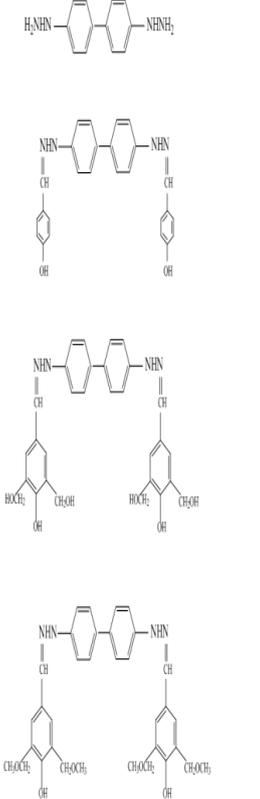
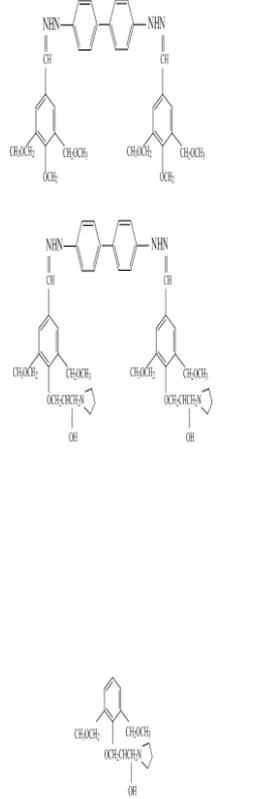
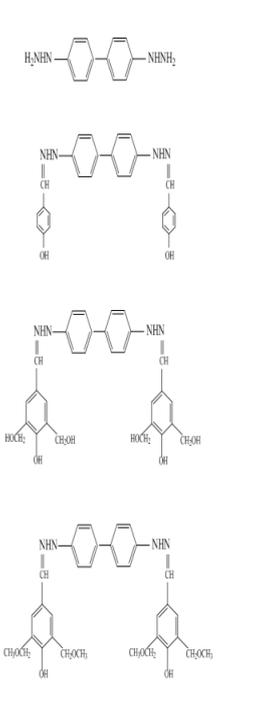
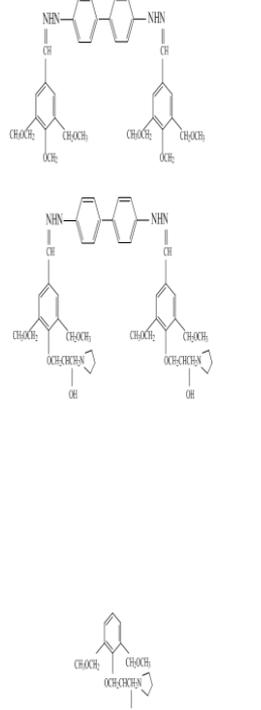
| | | | | | | |
|----------|---|--|---|---|--|--|
| <p>2</p> |  | <p>δ: (7.72)(Ar-H) δ: (10.1-10.9)(H,OH) δ: (9.7-9.8)(H,NH)</p> | <p>δ: (129.1-129.9) (aromatic carbons). δ: (115.2-115.3) (C,=CH) δ: (148.5-149.1) (C=N) δ: (155-156.3) (Ar-OH)</p> | <p>6</p>  | <p>δ: (7.2-7.5)(Ar-H) δ: (1.9-2.1)(3H,CH₃)</p> | <p>δ: (129.3-130.1) (aromatic carbons). δ: (2.1-2.3) (CH₂,oxarine) δ: (72.6-72.9) (C-O-C)</p> |
| <p>3</p> |  | <p>δ: (7.7-7.9)(Ar-H) δ: (10.3-11.1)(H,OH) δ: (1.05-2.20)(t,2H,CH₂)</p> | <p>δ: (126.5-126.8) (aromatic carbons). δ: (115.6-155.8) (C,=CH) δ: (154.8-154.9) (Ar-OH)</p> | <p>8</p>  | <p>δ: (7.8-7.9)(Ar-H) δ: (9.7-9.8)(H,OH) δ: (1.39-1.41)(2H,CH₂)</p> | <p>δ: (72.8-72.9) (C-O-C) δ: (129.3-130.1) (aromatic carbons).</p> |

Table 4:Depacited Elemental analysis (C.H.N) for some compounds

| No. | (C.H.N) analysis calculated (found) | | | Comp No. | (C.H.N) analysis calculated (found) | | |
|-----|-------------------------------------|----------------|------------------|----------|-------------------------------------|----------------|-----------------|
| | %C | %H | %N | | %C | %H | %N |
| 1 | 67.29 (68.29) | 6.54 (7.50) | 26.17 (27.18) | 4 | 68.23 (68.23) | 6.35 (7.33) | 9.37 (10.30) |
| 2 | 73.93 (74.93) | 5.21 (6.20) | 13.27 (14.30) | 6 | 66.86 (67.80) | 6.61 (7.16) | 8.21 (9.21) |
| 3 | 66.42 (67.40) | 5.54 (6.20) | 10.33 (11.33) | 8 | 65.53 (66.52) | 7.03 (8.04) | 9.52 (10.50) |

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تحضير وتشخيص بعض مشتقات قواعد شف الفينولية

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الخلاصة:

تم في هذه الدراسة تحضير سلسلة من مشتقات قواعد شف الايبوكسيه باستخدام المركب الأساس(4-ثنائي مركبتو-ثنائي الفينيل) بعد مفاعله مع الهيدرازين المائي (99% ليكون المشتق (1) الذي تم تحويله إلى قاعدة شف الفينولية، المشتق (2) والذي يعطي المشتق الميثولي (3) بعد تفاعله مع الفورمالديهايد بوجود هيدروكسيد الصوديوم. يتفاعل المشتق (3) مع الكحولات أعطى المشتقات الايثرية لقاعدة شف الفينولية (4) و (5)، وبمفاعلتها مع الايبي كلوروهيدرين تم الحصول على قواعد شف الايبوكسية (6) و (7). وأخيراً حضرت المشتقات الايبوكسية المفتوحة الحلقة بمفاعلة المشتقات (6) و(7) مع المورفلين بوجود الميثانول. شخّصت هذه المركبات جميعها باستعمال الطرق الطيفية FT-IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, (C.H.N), في مركز الاستشارات في الجامعة الأردنية.