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Synthesis and Thermal Electo Conductivity of Some New Triazole Derivatives Bearing Azo or Azomethain Group

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Abstract

Newly acid hydrazide was synthesized from ethyl 2-(2,3-dimethoxyphenoxy) acetate (**2**), which is cyclized to the corresponding 4-amino-1,2,4-triazole (**3**). Five newly azo derivatives (**4a-e**) were synthesized from this 1,2,4-triazole by converting the amine group to diazonium salt then reacted with various substituent phenol,as well three newly imine derivatives (**5a-c**) were synthesized from reacting the amine group of compound (**3)** with three aryl aldehyde. The thermal electro conductivity of these compounds was tested at 30, 50, 75 and 100 ^{o}C. compound **4a** showed interesting electro conductivity at 75^{o}C as well **5a** at 75^{o}C while **5b** showed significant conductivity at 100 ^{o}C.

Keywords: Triazole derivatives, Electro Conductivity, Azo, Azomethine

1.Introduction

Heterocyclic chemistry can be considered as a separated field in organic chemistry according to their many dictated of history with unboundary spectrum of applications. Triazole is one of the famous five membered ring with three nitrogen atoms[1]. During the last seventh decades many researchers have exhibited great interest with synthesis of 1,2,4-triazoles and particularly the 4-amino-1,2,4-triazoles derivative due to their interesting biological and pharmaceutical properties. For instance, some 1,2,4-triazoles showed antibacterial activity [2], anticancer [3], antioxidant[4], antifungal [5], Anti Leishmanial[6] and anti-inflammatory [7]. Furthermore, The 1,2,4-triazole showed divers physical properties such as electrochemical, spectro electrochemical [8, 9], corrosion inhibition of copper [10], as well inhibition of mild steel corrosion in hydrochloric [11], optical properties[12] and thermal conductivity [13]. Also the compounds which contain azo group and azomethine showed intensive interest in pharmacological and medicinal field besides they exhibited interested physical properties such as pH optical sensor[14], luminance and light-emitting diodes [15, 16] and electro conductive properties[17, 18]. According to the great importance of these compounds, this article presented synthesis of new 4-amino-1,2,4-triazole and their azo and azomethine derivative and investigated their thermal electro conductivity.

2.Experimental

2.1 General

The chemicals and solvents were utilized brand Sigma-Aldrich, Fisher and Merck to synthesize the target compounds without any purification. Uncorrected open capillary tube method was utilized to record the melting point by MEL-TEMP II instrument. Thin layer chromatography (silica gel TLC) plate brand Merck were used to determine the purities of these compounds and end of reaction. Either iodine vapors or UV lights were used to locate the spot. FTIR 600 was used to recognize the FTIR spectra. All NMR spectra were assigned NMR ready 60,60MHz spectrometer, DMSO-d6 was used as the solvent with TMS as internal standard. The element analysis (CHNS) was recognized by EURO EA 3000. The thermal electro conductivity of the synthesized compound was detected by LCR-8110G/8105G. All the analysis were carried out at Central Service Laboratory/ College of Education For Pure Science / Ibn Al-Haitham , University of Baghdad.

2.2 Synthesis of Ethyl 2-(2,3-dimethoxyphenoxy)Acetate 1.

Ethyl bromoacetate (16.7 g, 100mmol) was added dropwise to a stirring solution of 2, 3-dimethoxy phenol (15.4 g, 100 mmol) and potassium carbonate (13.8 g, 100 mmol) in dry DMF 100mL. The mixture was heated under refluxed at 70 ˚C for 24 hs. The reaction was followed by TLC using hexane: ethyl acetate (1:1) as eluent. After cooling the mixture was extracted by ethylacetate (2× 50 mL). The combine organic layer was dried under magnesium sulfate. After removal of the solvent under reduced pressure affords pale yellow liquid. Yield (83%) (19.9 g); FT-IR (KBr, υ_{max}): 3057, 3124 (CH_{Ar}), 2974, 2839 (CH_{Aliph}), 1755 (C=O), 1668, 1593 (C=C), 1236 (Ar-O-C), 1203 (C-O), 1119 (OCH_3-OCH_2) cm^{-1}; ^{1}H-NMR (DMSO-d_6, 60 MHz) ppm; 1.22 (t, 3H, CH_3) 3.60 (s, 3H, OCH_3), 3.64 (s, 3H,OCH_3), 4.19 (q ,2H ,O=C-CH_2), 4.62 (s, 2H, OCH_2), 6.36 -7.05 (m, 3H ,Ar-H) .

2.3 Synthesis of 2-(2,3di methoxyphenoxy)Acetohydrazide 2.

Excess of hydrazine hydrate (80%) was added to a stirring solution of Ethyl-2(2, 3-dimethoxyphenoxy) acetate) (19 g,79 mmol) in 40 mL of ethanol. The mixture was left under stirring overnight at ambient temperature. The solvent was reduced to half by evaporation under reduced pressure. The white solid precipitated was collected by filtration then washed with cold distilled water. The crud product was crystallized from methanol to afford white crystal yield (92%) (16.45 g): M.p.(104-106˚C); FT-IR (KBr, υ_{max}): 3427, 3325 (NH_2), 3286 (NH), 3097, 3032 (CH_{Ar}), 2999, 2835 (CH_{Aliph}), 1655 (C=O) 1597, 1441 (C=C), 1304 (C-N), 1263 (Ar-O-C), 1117 (OCH_3-OCH_2) cm^{-1}; ^{1}H-NMR (DMSO-d_6, 60 MHz,) ppm: 3.36 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 4.26 (bs, 2H, NH_2), 4.43 (s, 2H, OCH_2), 6.5-7.07 (m, 3H, Ar-H), 9.11 (bs, 1H, NH).

2.4 Synthesisof4-amino-3-((2,3-dimethoxyphenoxy)methyl)-1H-1,2,4-triazole-5(4H)thione.3.

Excess of carbon disulfide (about, 3ml) was added dropwise to a stirring solution of 2-(2,3-dimethoxyphenoxy) acetohydrazide (5 g, 22.1mmol) and potassium hydroxide (22.1 mmol) in absolute ethanol (30 mL) at ambient temperature .The resulting precipitated was filtrated then washed by diethyl ether and dried. The crud potassium 2-(2-(2,3-dimethoxyphenoxy)acetyl) hydrazine carbodithioate salt (5g, 14.7 mmol.) was refluxed with 5 mL hydrazine hydrate 80% for 7 hrs until no more evolving of hydrogen sulfide gas which is tested by lead acetate paper. After cooling the product was poured into 100 mL crush ice .The PH of solution was adjusted to acidic medium (pH= 4-5) using solution of 5% hydrochloric acid. The precipitate was filtrated, washed with cold water and dried under vacuum pressure .The precipitate was crystallized by methanol yield (70%), (2.9g): M.p.(162-164˚C) ; FT-IR (KBr, υ_{max}): 3435, 3263 (NH_2), 3215 (NH), 3066, 3026 (CH_{Ar}), 2968, 2837 (CH_{Aliph}), 2773 (C-SH), 1643 (C=N), 1601, 1496 (C=C), 1296 (C-N), 1259 (Ar-O-C), 1176 (C=S), 1103 (OCH_3-OCH_2) cm^{-1}; ^{1}H-NMR (DMSO-d_6, 60 MHz) ppm; 3.67 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 5.12 (s, 2H, OCH_2), 5.28 (bs, 2H, NH_2), 6.67-7.16 (m, 3H, Ar-H), 7.75 (bs, 1H, NH).

2.5 General synthesis of-3-((2,3-dimethoxyphenoxy)methyl)-4-((2 or 4-hydroxy-substiuted phenyl)diazenyl)-1H-1,2,4-triazole-5(4H)-thione.4a-4e.(5-9)

A cold solution (0-5 C) of sodium nitrite 0.7, 10.14mmol) in 3mL of distilled water was added dropwised with manual stirring to cold solution(0-5 C) of 4-amino-3-((2,3-dimethoxyphenoxy)methyl)-1H-1,2,4-triazole-5(4H)-thione (0.35 g, 1.24 mmol) in 25 ml 4N hydrochloric acid. This mixture was added dropwised with manual stirring to cold solution (0-5C).of 10.14 mmol of substituted phenol in 15 mL of 4N hydroxide sodium. The mixture was adjusted to neutralized pH, then the precipitated was collected by filtration, washed with distill water and dried. The crud product was recrystallized from methanol.

2.6 (3-((2, 3-dimethoxyphenoxy) methyl)-4-((2-hydroxy-3,4dimethoxyphenyl)diazenyl)-1H-1, 2, 4-triazole-5(4H)thione.4a).

The crude product was crystallized from methanol to obtain green precipitate Yield (72%), (0.4 g): M.p (215-216˚C); FT-IR (KBr, υ_{max}): 3263 (NH) , 3228 (OH), 3064, 3032 (CH_{Ar}), 2968, 2835 (CH_{Aliph}), 2771 (C-SH), 2139 (N=N), 1601, 1489 (C=N&C=C), 1375 (OH- in plane), 1296 (C-N), 1259 (Ar-O-C), 1176 (C=S), 1101 (OCH_3-OCH_2), 648 (OH-out of plane) cm-^{1}: ^{1}H NMR (DMSO-$d_{6,}$ 60 MHZ) ppm ;3.63 (s, 6H, 2 × OCH_3) 3.73 (s, 6H, 2 × OCH_3), 5.60 (s, 2H, OCH_2), 6.78-7.18 (m, 5H, Ar-H) 10.19 (s, 1H, OH), 13.61 (bs, 1H, NH).

2.7 (3-((2, 3-dimethoxyphenoxy) methyl)-4-((2-hydroxy-3-nitrophenyl)diazenyl)-1H-1, 2, 4-triazole-5(4H)-thione.4b).

The crude product was crystallized from methanol to obtain orange precipitate yield (56%), (0.3 g): M.p (192-194˚C); FT-IR (KBr, υ_{max}); 3431 (NH), 3228 (OH), 3064, 3030 (CH_{Ar}), 2968, 2835 (CH_{Aliph}), 2771 (C-SH), 2141 (N=N), 1603 (C=N and C=C), 1496 (NO_2), 1369 (OH- in plane), 1296 (C-N), 1259 (Ar-O-C), 1176 (C=S), 1107 (OCH_3-OCH_2), 650 (OH-out of plane) cm^{-1}; ^{1}H-NMR (DMSO-d_6, 60 Mhz) ppm:- 3.63 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 5.60 (s, 2H, OCH_2), 6.80- 7.35 (m, 6H, Ar-H), 13.81 (bs, 1H, NH).

2.8 (3-((2, 3-dimethoxyphenoxy)methyl)-4-((2-hydroxy-4,5-dimethyl phenyl)diazenyl)-1H-1,2,4-triazole-5(4H)-thione.4c).

The crude product was crystallized from methanol to obtain dark brown precipitate yield (74%), (0.38 g): M.p (172-174˚C); FT-IR (KBr, υ_{max}): 3427 (NH), 3228 (OH), 3064, 3030 (CH_{Ar}), 2968, 2835 (CH_{Aliph}), 2771 (C-SH), 2119 (N=N), 1601, 1496 (C=N & C=C), 1365 (OH- in plane), 1296 (C-N), 1259 (Ar-O-C), 1228 (C=S), 1107 (OCH_3-OCH_2), 650 (OH-out of plane) cm^{-1}; ^{1}H-NMR (DMSO-d_6, 60 MHZ) ppm:-2.0 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 3.62

(s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 5.07 (s, 2H, OCH_2), 6.77-7.11 (m, 5H, Ar-H), 9.53 (bs, 1H, OH), 13.82 (bs, 1H, NH).

2.9 (3-((2, 3-dimethoxyphenoxy)methyl)-4-((4-hydroxy-3,5-dimethoxyphenyl)diazenyl)-1H-1, 2, 4-triazole-5(4H)-thione.4d).

The crude product was crystallized from methanol to obtain orange precipitate yield (70%) (0.39 g) : M.p (210-212˚C); FT-IR (KBr, υ_{max}): 3417 (NH), 3232 (OH), 3064, 3030 (CH_{Ar}), 2968, 2835 (CH_{Aliph}), 2769 (C-SH) ,2117 (N=N), 1604, 1496 (C=N & C=C), 1369 (OH- in plane), 1296 (C-N), 1259 (Ar-O-C), 1176 (C=S), 1103 (OCH_3-OCH_2), 648 (OH-out of plane) cm^{-1}; ^{1}H-NMR (DMSO-d_6, 60 MHZ) ppm:- 3.60 (s, 6H, 2 × OCH_3), 3.77 (s, 6H, 2 × OCH_3), 5.22 (s, 2H, OCH_2), 6.65-7.01 (m, 3H, Ar-H), 7.14 (s, 2H, Ar-$H_{syringic}$), 9.34 (bs, 1H, OH), 14.06 (bs, 1H, NH).

2.10 (3-((2, 3-dimethoxyphenoxy)methyl)-4-((4-hydroxy-3,5-dimethylphenyl) diazenyl)-1H-1,2,4-triazole-5(4H)thione.4e).

The crude product was crystallized from methanol to obtain pale yellow precipitate yield (75%) (0.38 g) : M.p (156-157˚C); FT-IR (KBr, υ_{max}); 3429 (NH), 3201 (OH), 3066, 3005 (CH_{Ar}), 2941, 2837 (CH_{Aliph}), 2775 (C-SH), 2141 (N=N), 1603, 1479 (C=N & C=C), 1356 (OH- in plane), 1296 (C-N), 1255 (Ar-O-C), 1178 (C=S), 1105 (OCH_3-OCH_2), 623 (OH-out of plane) cm^{-1}; ^{1}H-NMR (DMSO-d_6, 60 MHZ) ppm:- 2.21 (s, 6H, 2 × CH_3), 3.67 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 5.04 (s, 2H, OCH_2), 6.70-6.95 (m, 5H, Ar-H), 8.37 (bs, 1H, OH), 13.79 (bs, 1H NH).

2.11 General synthesis of 3-((2,3-dimethoxyphenoxy)methyl)-4-((arylidene)amino)-1H-1,2,4-triazole-5(4H)-thione.5a-5c.(11-13)

An ethanolic solution of aryl aldehyde (1.24 mmol) was add dropwise to a solution of 4-amino-5-((2,3methoxyphenoxy)methyl) (2,4)-dihydro-3-H (1,2,4)-triazole-3-thione (0.35 g , 1.24 mmol) in 2mL of ethanol in the presence of three drops of glacial acetic acid. The mixture was heated under reflux (50-60 °C) overnight. The precipitated was filtrated, dried and purified by crystallization utilizing suitable solvent.

2.12 (3-(2,3-dimethoxyphenoxy)-4-((3-nitrobenzylidene)amino)-1H-1,2,4-triazole-5(4H)-thione.5a).

The crude product was crystallized from methanol to obtain pale yellow precipitate yield (76%), (0.4 g) : M.p.(204-206˚C); FT-IR (KBr, υ_{max});3435 (NH), 3230, 3084 (CH_{Ar}), 2939, 2835 (CH_{Aliph}), 2752 (C-SH),1633, 1603 (C=N & C=C), 1531, 1354 (NO_2), 1294 (C-N), 1259 (Ar-O-C), 1174 (C=S), 1105 (OCH_3-OCH_2) cm^{-1}; ^{1}H-NMR (DMSO-d_6, 60 MHz) ppm: 3.50 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 5.19 (s, 2H, OCH_2), 6.58-6.95 (m, 3H, Ar-H), 7.46-7.89 (m, 4H, Ar-H), 9.98 (s, 1H, CH=N), 14.09 (bs, 1H, NH).

2.13 (3-((2, 3-dimethoxyphenoxy) methyl)-4-((4-hydroxy-3,5-dimethoxybenzylidene)amino)-1H-1,2,4-triazole-5(4H)-thione.5b).

The crude product was crystallized from methanol to obtain white precipitate yield (69%) (0.38 g) : M.p.(195-196˚C); FT-IR (KBr, υ_{max}): 3369 (OH), 3221 (NH), 3057, 3005 (CH_{Ar}), 2962, 2839 (CH_{Aliph}), 2762 (C-SH) 1583, 1514 (C=N & C=C), 1371 (OH- in plane), 1323, 1290 (C-N), 1254 (Ar-O-C), 1178 (C=S), 1115 (OCH_3-OCH_2), 646 (OH-out of plan) cm^{-1};

^{1}H-NMR (DMSO-d_6 , 60 MHz) ppm; 3.54 (s, 3H, OCH_3), 3.71 (s, 9H, 3 × OCH_3), 5.16 (s, 2H, OCH_2), 6.58-6.94 (m, 3H, Ar-H), 7.08 (s, 2H, Ar-H), 9.27 (bs, 1H, NH), 9.60 (s, 1H, CH=N), 14.00 (bs, 1H, OH).

2.14 (4,4-(1,4-phenylenebismethan-1-yl-1-ylidene))bis(azan-1-yl-1-ylidene) bis(3-((2,3dimethoxyphenoxy)methyl)-1H-1,2,4-triazole-5(4H)-thione.5c).

The crude product was crystallized from chloroform to obtain yellow precipitate yield (61%). (0.5 g) : M.p.(185-186°C); FT-IR (KBr, υ_{max}): 3435 (NH), 3188, 3001 (CH_{Ar}), 2964, 2831 (CH_{Aliph}), 2763 (C-SH), 1597, 1495 (C=N & C=C), 1298 (C-N), 1257 (Ar-O-C), 1173 (C=S), 1109 (OCH_3-OCH_2) cm^{-1}; ^{1}H-NMR (DMSO-d_6, 60 MHz) ppm ; 3.50 (s, 6H, 2 × OCH_3), 3.66 (s, 6H, 2 × OCH_3), 5.23 (s, 4H, 2× OCH_2), 6.69-6.96 (m , 6H, Ar-H), 7.88 (s, 4H, Ar-H), 10.14 (s, 2H, 2 × CH=N), 14.12 (bs, 2H, 2× NH).

2.15 Thermal Electro Conductivity Test

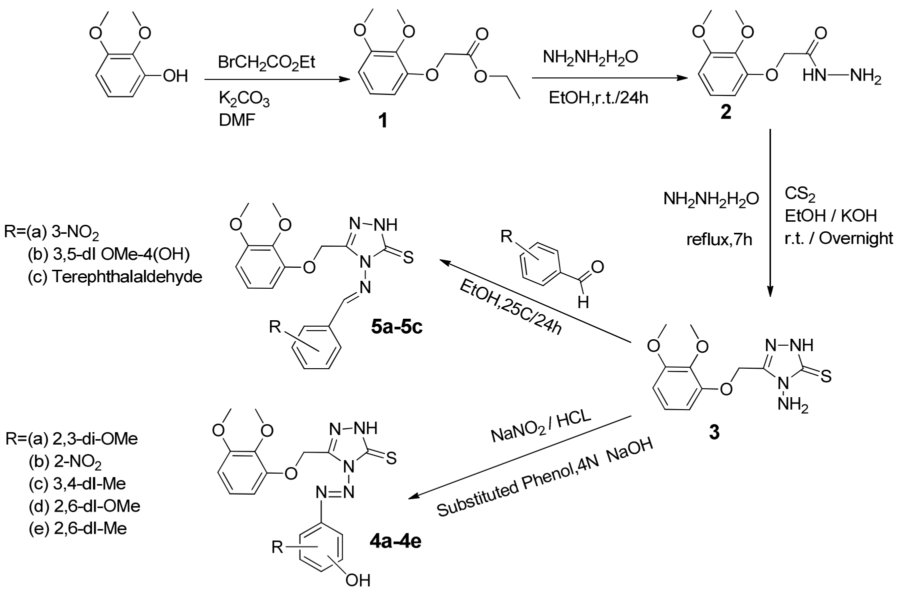
The target samples were formed by pressing 0.2 g from pure material to thickness 0.08 cm and 1cm as diameter under 20 Mpa.(Mega pascal) The conductivity was detected by LCR meter at 50-300000 Hz at 30, 50, 75 and 100 °C. The electrical capacity and the tangent of loss angle were determined also electrical conductivity was determined from the following equations [19].

$C_v=\varepsilon_0 A/d$
$\varepsilon_r'=C_P/C_0 \longrightarrow C_p d/ \varepsilon_0 A$
$\varepsilon_r''= \varepsilon_r' \tan(\delta)$
$\sigma_{a.c}=\omega\, \varepsilon_r''\, \varepsilon_0$
where
Cp = Capacitor Materials
A = Area
d = distance
C_0 =Capacity in vacuum
ω = Angular frequency

$\sigma_{a.c}$ = Alternating electrical conductivity
$\tan(\delta)$ = Tangent of loss angle
ε_0 = Permittivity of vacuum
ε_r' = Permittivity of the material
ε_r'' = Relative permittivity

3.Result and Discussion

Newly 4-amino-1,2,4-triazole and their azo and azomethine derivative were synthesized as depicted in Scheme (1) and characterized by FTIR, ^{1}H-NMR spectra and C.H N analysis.



Scheme 1. Synthetic route of newly compounds 1-5a-c.

Ethyl 2-(2,3-dimethoxyphenoxy)acetate (1), was synthesized from reaction ethyl bromoacetate with of 2, 3-dimethoxyphenol in DMF in the presence of potassium carbonate as scavenger. The target compound was characterized by FT-IR and ^{1}H-NMR. The FT-IR spectrum exhibited disappearance the OH group of phenol and recorded new band at 1755 cm^{-1}attributed to the carbonyl group. The band located at 1668 and 1593 cm^{-1} assigned to C=C. Moreover, the band at 1236 cm^{-1}was assigned to Ar-O-C. Besides to the aromatic and aliphatic CH were assigned at their expected 3057, 2839 cm^{-1} .The 1H-NMR recorded triplets signal at (1.22) ppm attributed to CH_3 group at ester while the CH_2 group of ester appeared at (4.19) ppm as quartet. Also the OCH_2 group attached to carbonyl was appeared as singlet peak at (4.62) ppm. The two methoxy group and the protons of phenyl ring appeared at expected area as depicted in **Figure 1**. The corresponding acid hydrazide (2) was synthesized from reaction of the Ethyl-2(2, 3-dimethoxyphenoxy) acetate with excess hydrazine hydrate (3 equivalents) in ambient temperature. This compound was characterized by FT-IR and ^{1}H-NMR spectra. The FT-IR spectrum showed disappearing of ester carbonyl and new band appeared at 1655 cm^{-1} attributed to hydrazide carbonyl as well the band of NH_2 and NH of the hydrazide appeared at 3427, 3325 and 3286 cm^{-1} respectively. The band at 1626 cm^{-1} attributed NH bending. The ^{1}H-NMR spectrum exhibited disappearing of ethoxyl group of ester and appearing of new broad peaks at (4.26) and (9.11) ppm respectively attributed to protons NH_2 and NH of Hydrazide group. The methoxy protons were displayed as singlet peak at (3.36) and (3.72) ppm, while the peak of OCH_2 appeared at (4.43) ppm as singlet peak. The aromatic peaks appeared as multiplet peaks at (6.5-7.07) ppm. The 1,2,4-triazole was synthesized by two steps. The first step was synthesis of potassium 2-(2-(2,3-dimethoxyphenoxy)acetyl)hydrazine carbodithioate form reacted the corresponding hydrazide (2) in absolute ethanol with carbon disulfide at ambient temperature. The corresponding potassium salt was cyclized to 1,2,4-triazole utilizing hydrazine hydrate. This compound was characterized by FT-IR and ^{1}H-NMR spectra. The FT-IR of the resulting compound displayed band at 3435 and 3263 cm^{-1} for NH_2 and the band at 3215 cm^{-1}for NH .The aromatic and aliphatic CH exhibited at 3066, 2837cm^{-1}. The SH band was located as weak band at 2773cm^{-}

^{1} and the C=S located at 1176 cm^{-1}due to tautomerism between thione- thiol fact[20]. The C=N band appeared at 1643 cm^{-1}. The ^{1}H-NMR spectrum exhibited two singlet at (3.67-3.77) ppm for two OCH_3 group and singlet peak at (5.12) ppm for OCH_2. The peak of NH_2 appeared as broad singlet at (5.28) ppm. The three aromatic protons appeared as multiplet peak at (6.67-7.16) ppm as well the peak at (7.75) ppm assigned to NH as depicted in **Figure 2**. Five new Azo compounds (4a-4e) were synthesized from reaction the 1,2,4-triazole-4-anine (3) with nitrozo acid to form the corresponding diazonium salt. The resulting diazonium salt reacted with five different substituted sodiume phenoxide at low temperature (0-5 ^{o}C). These compounds were characterized from their FT-IR and^{1}H-NMR spectra.

The FT-IR spectra exhibited disappearance the band of NH_2, which is considered good evidence for success the reaction. The band of azo group was assigned at 2141-2117 cm^{-1} for (4a-4e**)**. Furthermore the FTIR spectra for these compounds exhibited the C=N and C=C at 1604-1479 cm^{-1} the band of NH and OH were detected at 3431-3263 cm^{-1} and 3232-3201 cm^{-1} respectively. The aromatic and aliphatic C-H were appeared at 3066-3005 cm^{-1} and 2968-2835 cm^{-1} respectively. In addition to the FTIR spectra, the ^{1}H-NMR spectra confirm formation of the new proposed structures for compounds (4a-4e**)**. The ^{1}H-NMR exhibited disappearing of the broad peak which belonged to protons of NH_2. Furthermore, rising new peaks attributed to the substituted phenol besides to the proton of hydroxyl group of phenol at (8.37-10.19) ppm. The ^{1}H-NMR spectrum of compound (4b**)** displayed the two singlet peaks at (3.63) and (3.73) ppm for six protons of two groups of OCH_3. The two protons of OCH_2 appeared as singlet at (5.60) ppm. The aromatic protons showed multiplet signal due to over lapping and showed integration for six protons. The OH of phenolic hydroxyl was appeared at (10.19-8.37) ppm. In spite of the proton of hydroxyl group of 2-nitrophenol (4b) did not recognize at the ^{1}H-NMR spectrum, that can be referred the intramolecular hydrogen bonding and to the deuterium exchange [21]. The proton of NH for the triazole ring was assigned at (13.61-14.06) ppm.

The ^{1}H-NMR of compound (4a) and showed the integration of protons of methoxy group equal twelve protons , while the integration of protons OCH_2 group remained equal to two protons, that refer to two new methoxy group as substituent of phenol. The OH of phenol of this compound appeared at (10.19) ppm respectively The ^{1}H-NMR spectrum of compound (4c) showed the methyl as substituent group of phenol at (2.0) ppm for 2× CH3 and (2.23) ppm for 2× CH_3 respectively. **Figure 3.** depected the ^{1}H-NMR spectrum of compound (4c) **Table 1.** showed some selective physical properties

Table 1. Tabulated Some physical properties of these compounds (4a-4e).

No.	R	M.P	Yield	M.F	Color
4a	2,3-di-OH	215-216℃	72%	$C_{19}H_{21}O_6N_5S$	Green
4b	2-NO_2	192-194℃	56%	$C_{17}H_{16}O_6N_6S$	Orange
4c	3,4-di-Me	172-174℃	74%	$C_{19}H_{21}O_4N_5S$	Dark brown
4d	2,6-di-OMe	210-212℃	70%	$C_{19}H_{21}O_6N_5S$	Orange
4e	2,6-di-Me	156-157℃	75%	$C_{19}H_{21}O_4N_5S$	Pale yellow

These compounds (5a-5c) were synthesized from reaction of the triazole and arylaldehyde in the presence of glacial acetic acid as catalyst. **Table 2.** showed some selective physical properties.

Table 2. Tabulated some physical properties of these compounds (5a-5c).

No.	R	M.P	Yield	M.F	Color
5a	3-NO_2	204-206℃	76%	$C_{18}H_{17}O_5N_5S$	Pale yellow
5b	3,5-di-OMe-4-OH	195℃	69%	$C_{20}H_{22}O_6N_4S$	White
5c	Terephthalaldehyde	185-186℃	61%	$C_{30}H_{30}O_6N_8S_2$	Yellow

These compounds characterized from their FT-IR and ^{1}H-NMR spectra. The FT-IR showed disappearance the band of NH_2 from 3435-3263 cm^{-1}. The compound (5a) showed new absorption band at 1531-1354 cm^{-1} for symmetrical and asymmetrical absorption of NO_2. Compound (5b) exhibited band at 3369 cm^{-1} for OH. Moreover, compound (5c) displayed the NH band at 3435 cm^{-1}. The band of C=N appeared in same region of C=C and that result was in agreement with literatures [22-25].

The ^{1}H-NMR exhibited disappearance the broad signal for NH from (9.27-14.12) ppm and appearance new characterized peak at (9.60-10.14) ppm for CH=N with integral of one proton. Furthermore, the integration of aromatic was in agreement with proposed structure besides to the protons of two methoxy groups and the protons of OCH_2 group attached 1,2,4-triazole ring at position three were appeared at their expected regions. For example, the ^{1}H-NMR spectrum of compound (5c) as shown in **Figure 4**.

The spectrum showed two singlet peaks at (3.50) and (3.66) ppm respectively for twelve protons of four OCH_3 groups. The singlet peak located at (5.23) ppm with small shoulder, for four protons of two groups of OCH_2. The aromatic region showed multiplet at (6.69-6.96) ppm for six protons while the for protons of 1,4-phenylene group were located as singlet signal with small shoulder. The shoulders for protons of OCH_2 group and 1,4-phenylen group could be attributed to geometric tautomerism [26] which affected at the electronic environment of protons of 1,4-phenylene attached with imine group [27]. The two protons of bis imine group appeared at low field (10.14) ppm and that could be attributed to long chine conjugated and to existence of imine-enamine tautomerism[28]. The peak of NH was assigned at (14.12) ppm. The found percentages of C.H.N.S analysis were in agreement with calculated percentages as tabulated in **Table 3**.

3.1 Electro Thermal Conductivity

Compounds (4b) and (4c) did not exhibit any notable conductivity, while compounds (4d) and (4e) exhibited low electro conductivity less than (0.0002 $(\Omega.m)^{-1}$ at 30°C, as depicted in **Figure 5**.

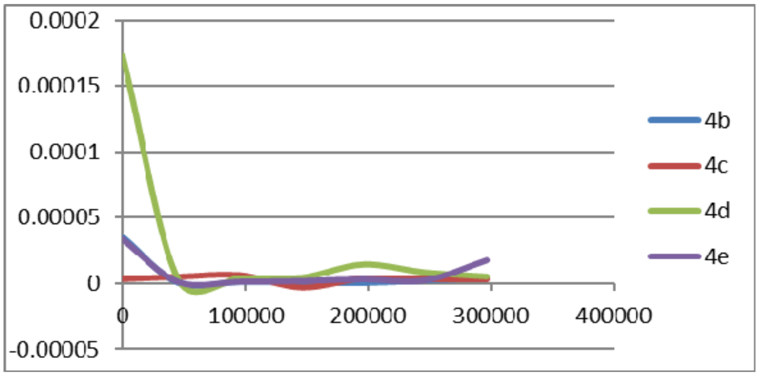


Figure 5. Thermal electro conductivity of compounds (4b-4e) at 30◦C.

Interested electro conductivity has been observed with compound (4a) at frequency between 50Hz to 1MHz 30◦C. as demonstrated in **Figure 6**.

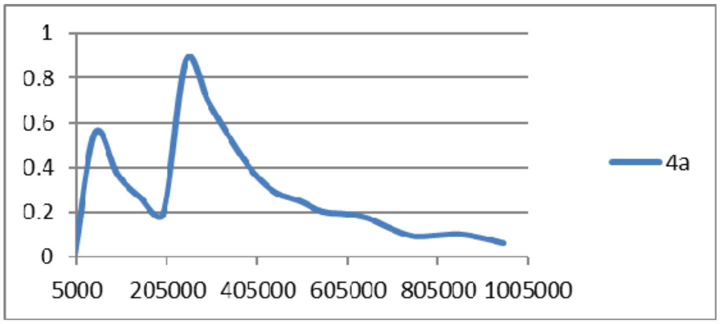


Figure 6. Thermal electro conductivity of compounds (4a) at 30◦C.

This group of compounds did not exhibit any notable chance at 50◦ C and showed same regular demeanor with 30◦C, when the conductivity tested at 75◦C Also, compounds (4b-e) still exhibited same electro properties as it exhibited in 30◦ C,. in another hand, compound (4a) was exhibited unexpected demeanor as depicted in **Figure 7.**

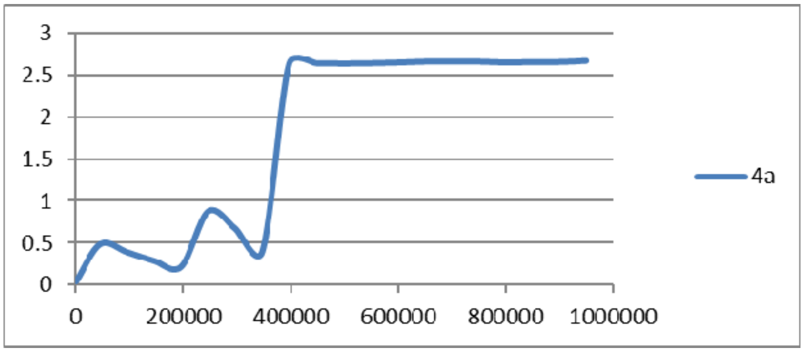


Figure 7. Thermal electro conductivity of compounds (4a) at 75◦C.

The electro thermal conductivity of these compounds at 30º C was demonstrated in **Figure 8**. Compound (3) do not exhibite any electro conductivity in different temperatures at frequency range 50-300000 Hz. Compound

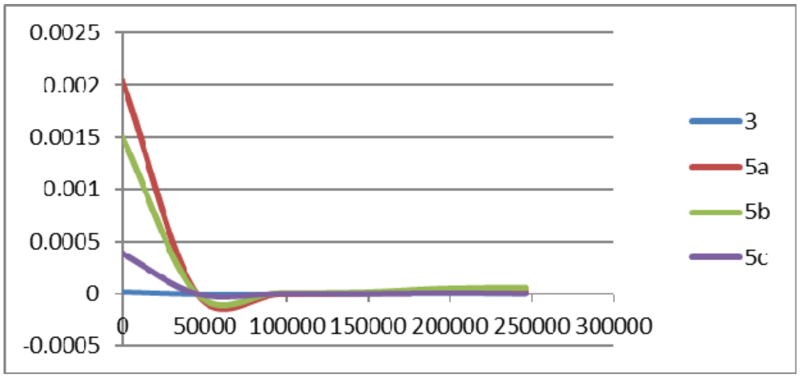


Figure 8. Thermal electro conductivity of compounds (3-5a-c) at 30°C.

Compound 5a exhibited the highest conductivity at 30 °C and this conductivity increased at 50°C and 75 °C. The sequence of the electro conductivity of these compounds was changed at 100°C. The electro conductivity of compound 5b to be the forefront and the electro conductivity 5a was decreased. As demonstrated at **Figure 9.** and **10**.

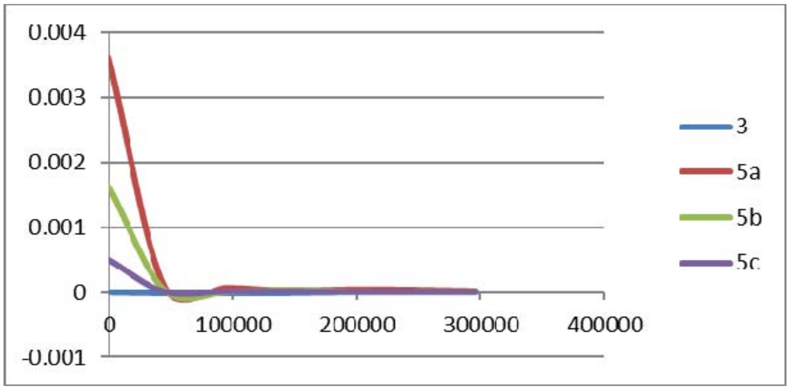


Figure 9. Thermal electro conductivity of compounds (3-5a-c) at 50°C.

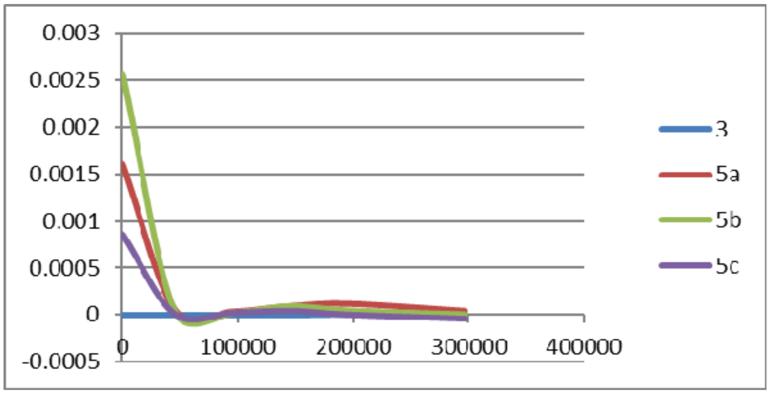


Figure 10. Thermal electro conductivity of compounds (3-5a-c) at 100°C.

4.Conclusion

Two newly series from 4-amino-1,2,4-triazole derivatives (4a-e and 5a-c) were successfully synthesized and characterized. The thermal electro conductivity were screened at 30, 50, 75 and 100 °C. compound 4a exhibited interested conductivity at 30-75 °C. Furthermore, compound 5a showed significant thermal electro conductivity at 30, 50 and 75 °C, while compound 5b showed interested electro conductivity at 100 °C.

Table 3. CHNS analysis of compounds (3-5c)**.**

Com No	M.F	Theoretical	Practical
3	$C_{11}H_{14}O_3N_4S$	C-46.80 H-500 N-19.85 S-11.36	C-46.72 H-5.1 N-19.66 S-10.92
4a	$C_{19}H_{21}O_6N_5S$	C-51.00 H-4.73 N-15.65 S-7.17	C-51.12 H-5.09 N-15.98 S-7.09
4b	$C_{17}H_{16}O_6N_6S$	C-47.22 H-3.73 N-19.44 S-7.42	C-47.31 H-3.89 N-19.56 S-7.32
4c	$C_{19}H_{21}O_4N_5S$	C-54.93 H-5.09 N-16.86 S-7.72	C-55.01 H-5.26 N-17.1 S-7.62
4d	$C_{19}H_{21}O_6N_5S$	C-51.00 H-4.73 N-15.65 S-7.17	C-51.14 H-5.11 N-15.93 S-6.99
4e	$C_{19}H_{21}O_4N_5S$	C-54.93 H-5.06 N-16.86 S-7.72	C-55.02 H-5.21 N-17.08 S-7.61
5a	$C_{18}H_{17}O_5N_5S$	C-52.04 H-4.12 N-16.86 S-7.72	C-52.12 H-4.37 N-17.04 S-7.38
5b	$C_{20}H_{22}O_6N_4S$	C-53.80 H-4.97 N-12.55 S-7.18	C-53.67 H-5.39 N-12.84 S-7.09
5c	$C_{30}H_{30}O_6N_8S_2$	C-54.37 H-4.56 N-16.91 S-9.66	C-54.55 H-5.82 N-17.06 S-9.53

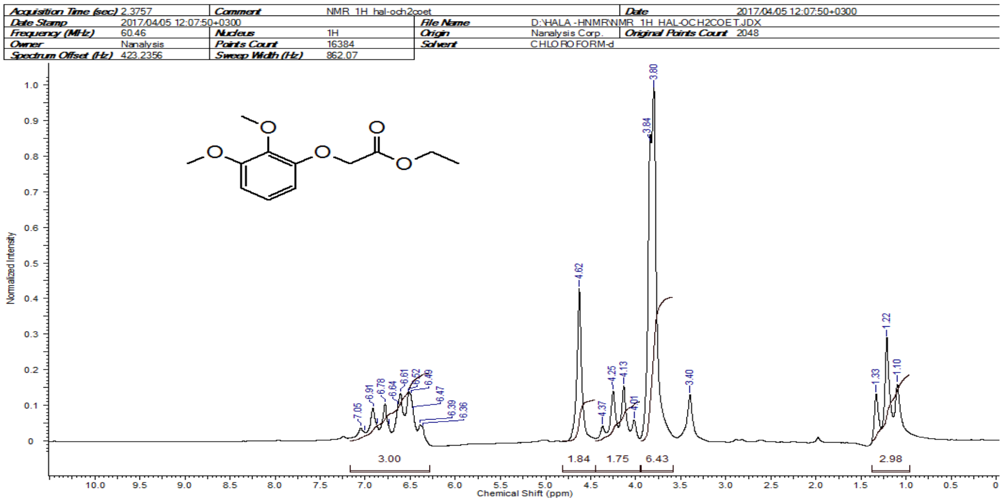


Figure 1. ^{1}H-NMR (60 MHz, DMSO-d$_6$) spectrum of compound 1.

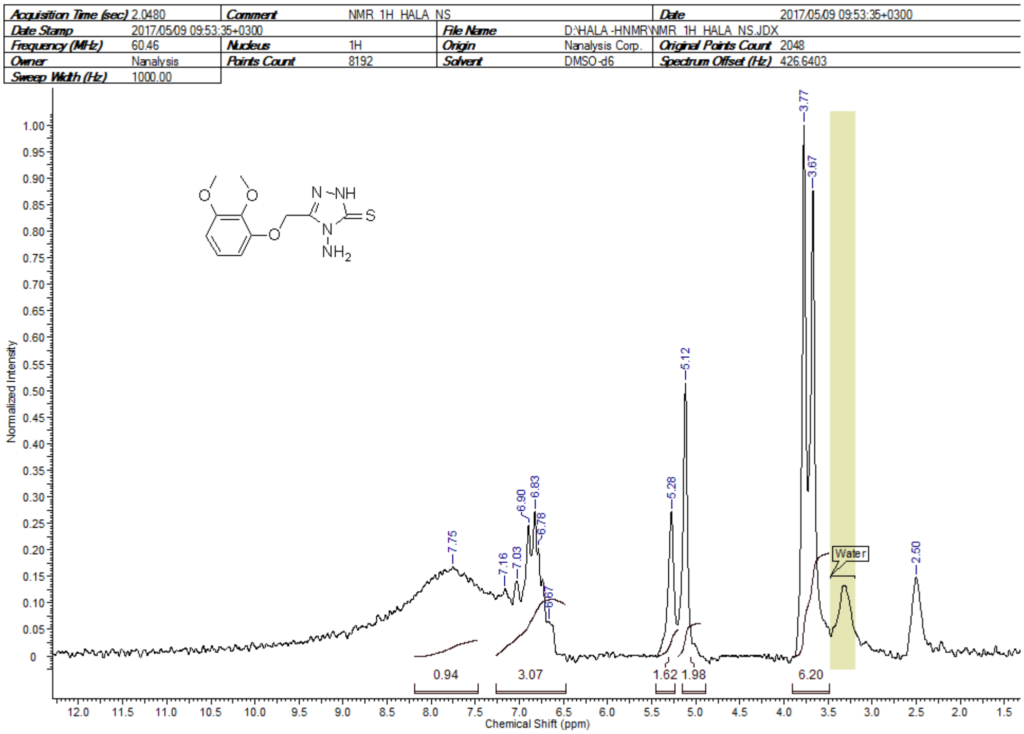


Figure 2. ^{1}H-NMR (60 MH$_Z$, DMSO-d$_6$) spectrum of compound 3**.**

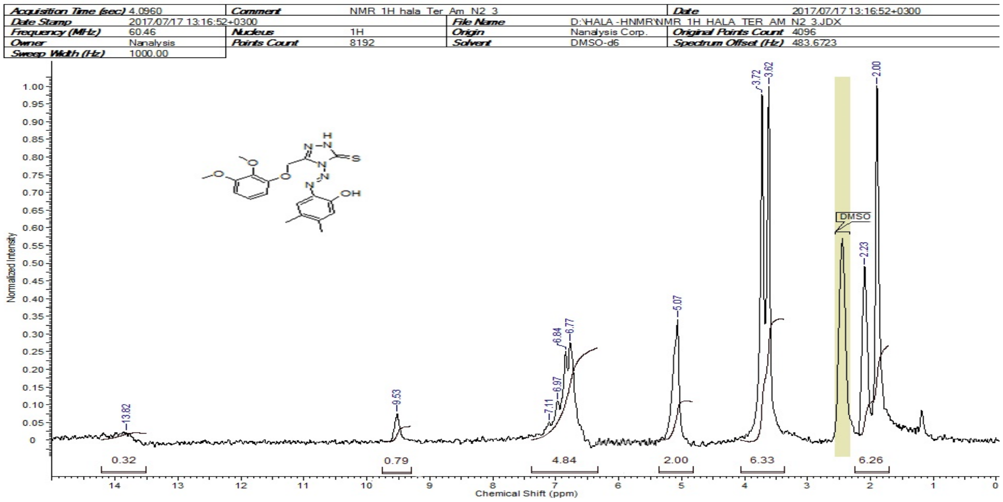


Figure 3.^{1}H-NMR (60 MH$_Z$, DMSO-d$_6$) spectrum of compound 4c

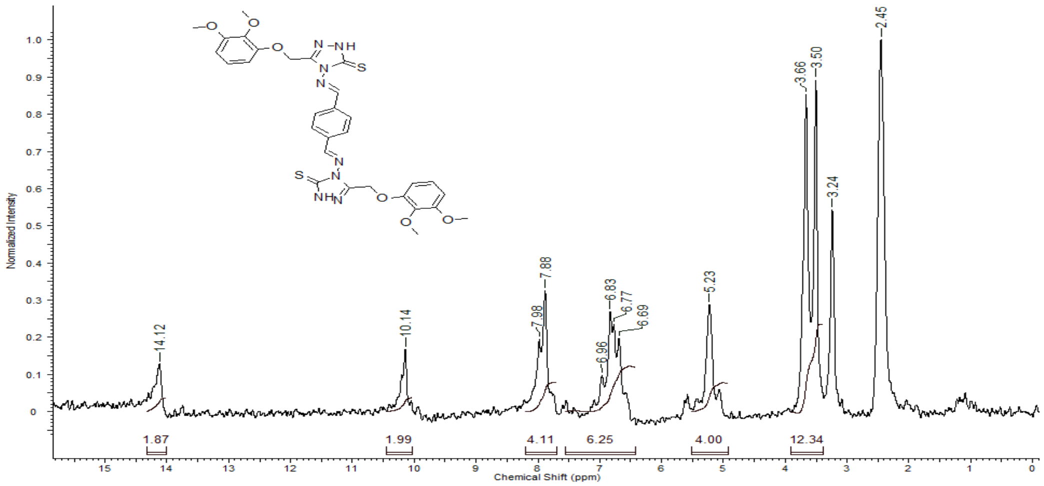


Figure 4. ^{1}H-NMR (60 MH$_Z$, DMSO-d$_6$) spectrum of compound 5c .

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