

Synthesis and Characterization of Some New Substituted 1,3,4- Thiadiazole and Their Derivatives

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Abstract

Several 2-amino-5-(3,4-dihydroxy phenyl-azo-benzen)l ,3,4-thiadiazole and some 2-substituted benzyldineamino-s(3,4-dihydroxy phenyl-|oaz-benzenl-1,3,4-thiadiazoles were prepared as possible biologically active agents.-the FT-IR and nuclear magnetic resonance of these compounds are reported.

1-introduction :

1,3,4-thiadiazole and their derivatives constitute an important class of organic compounds with divers agricultural, industrial and biological activates(1-3),including anti-microbial(4,5),sedative ,anti-convulsant(6,7) and anti- inflammatory(8).In addition many derivatives of aniline that had been used as dyes(6).

In this work 2-amino-5-(3,4-dihydroxy phenyl-azobenzene)-1,3,4-thiadiazole (11) has been synthesized from the reaction of 3,4-dihydroxyphenyl-azo-benzoic acid with phosphorus oxychloride .Also some 2-substituted benzyllidinamino -5- (3,4- dihydroxyphenyl -azo-benzene) l ,3,4-thiadiazoles (111) have been synthesized from (11) and the corresponding p-substituted aldehydes.

2-Experimental :

1-Melting points was determined using an electrothermal digital melting point apparatusand are uncorrected.

2-FT-IR spectrum were recorded on Thermo Mattson FT-IR500 spectrophotometer using potassium bromide discs .

3-H NMR spectra were recorded on Br uker 200 MHz - spectrophotometer with chemical shifts reported in O units DMSO was used as a solvent.

2.1- Preparation of 3,4- dihydroxypheny l-azo- benzoic acid (1) : This compound has been synthesized according to the literature (9) by dislocation of p-amino benzoic acid at low temperature and coupling the diazonium salt formed with catechol in 10% potassium hydroxide solution.-the isolated red dye washed with water and recrystallized from ethanol.Melting

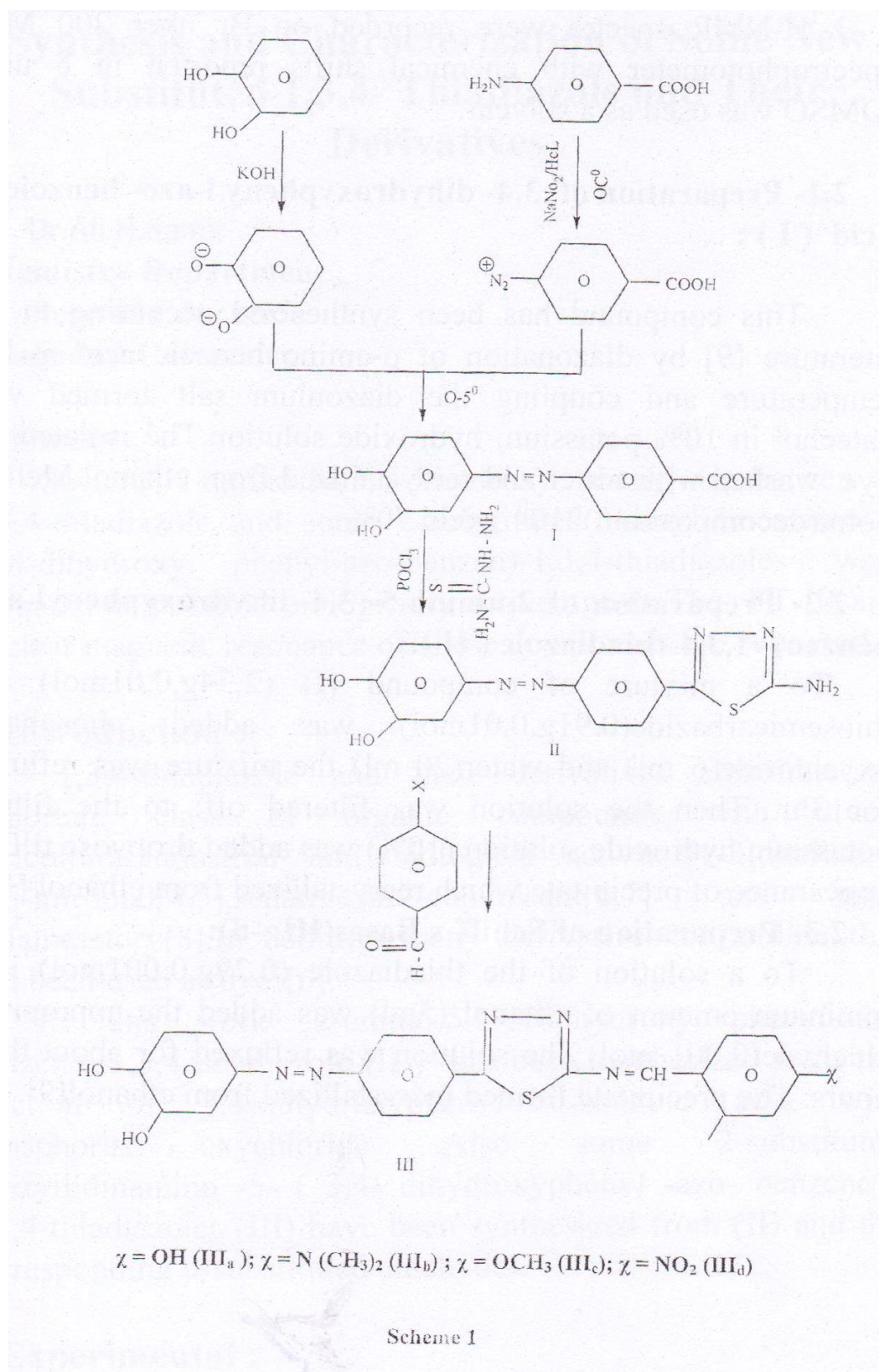
pointtdecomposition)210o; yield70%

2.2- Preparation of 2-amino-5-(3,4-dihydroxyphenyl-azobenzen) -1,3,4-thiadiazole (11):

To a mixture of compound (1) (2.34g,0.01mo1) and thiosemicarbazide(o.9lg,o.0lmol) was added phosphorus oxychloride(6 ml) and water(2o ml) the mixture was reflexed for 3hr. Then the solution was filtered off; to the filtrate potassium hydroxide solution (10%) was added dropwise till the appearance of precipitate, which recrystallized from ethanol (10)

2.3- Preparation of Schiff 's Bases(IIIa-d):

To a solution of the thiadiazole (0.29g,0.001mo1) in a minimum amount of ethanol (5m1) was added the appropriate aldehyde(o.ool mol).-the solution was refluxed for about three hours. The precipitate formed recrystallized from ethanol(9).



3-Results & Discussion:

The melting points, yields ,and colors of the synthesized compounds

II,111a-d are summarized in table 1 .

3.1- FT-IR Spectra (11-13) :

FT- IR spectrum (cm^{-1} potassium bromide);

1- The FT-IR spectrum of compound 11 (figure 1) shows the disappearance of the bands ascribed to C=O and OH (of COOH group) stretching and appearance of a new band at 3293cm^{-1} (doublet) and at 1604 cm^{-1} attributed to NH stretching and bending respectively. A strong band at 1668 cm^{-1} assigned to C=N (of thiadiazole ring) scratchiest medium peak at 604 cm^{-1} assigned to CS stretching .other bands being at 3105 cm^{-1} at 3552 cm^{-1} assigned to O-H stretching ,and at 819 cm^{-1} assigned to CH (aromatic) stretching and out of plane bending respectively.,at $1586,1532\text{ cm}^{-1}$ assigned N=N and C=C (aromatic) stretching ;at $1393,1308,1254\text{ cm}^{-1}$ assigned to CN stretching and CO stretching.

2- The FT- IR spectrum of compound IIIb (figure 2) , shores the disappearance of the bands attributed to NH stretching and ben ding and the appearance of new bands at 2914 cm^{-1} . and 2822 cm^{-1} assigned to CH (of CH_3 group) asymmetric and symmetric stretching respectively and medium band at 2714cm^{-1} assigned to N- CH_3 stretching (13).A strong band at assigned to N- CH_3 stretching to C=N (imine group) stretching,in 1660 cm^{-1} assigned addition to other band stop 3314 cm^{-1} assigned to OH stretchiest very strong band at $1598,1540$ and 1533 cm^{-1} assigned to C=C (aromatic)and N=N stretching at $1371,1335\text{ cm}^{-1}$ C-O stretching ;at 824 and 1232 cm^{-1} assigned to CN an 812 cm^{-1} assigned to CH(aromatic-H to out of the plane bending at 595 cm^{-1} assigned to CS stretching)

3.2- ^1H NMR Spectra [11 13] ^1H NMR spectrum (δppm ,DMSO- d_6) :

1- ^1H NMR spectrum of compound I (figure 3) shows the expected structure; singlet at 12.4 and 10.3 assigned to -COOH and -OH- ortho respectively; the single attributed to OH-para dose not appear because it is covered by DMSO solvent signal is As shown by figure 4 the signals assigned to aromatic - H could be estimated as following :a doublet at 8.07 (2H)with $j_1=6\text{ Hz}$ and a doublet at 7.9 (2H)with $j_1=6\text{ Hz}$.Therefore j_1 is the coupling between the vicinal protons c,d.Doublet at 7.68 with $j_2=8\text{ Hz}$; a doublet -doublet at 6.5 (1H)with $j_2=8\text{ Hz}$ and $j_3=3\text{ Hz}$.-Therefore j_2 is the coupling between the vaginal protons e,f, and J_3 is the coupling between the meta protons f. and g.

¹H NMR spectrum of compound IIIa (figure 5) shows a
 2-The singlet at 10.3 assigned to intramolecularly bonded OH proton (two broad signals of the same shape at 8.24 attributed to the vicinal aromatic (1H) of the middle ring B; it seems that the coupling constant is so small that each signal is not shown as a doublet as expected the sharp singlet at 8.37 is assigned to CH=N proton. -the two doublet doublet at 8.045 and 7.20 are assigned to the vicinal aromatic (1H) of the terminal rings (A and C) the former is assigned to the protons ortho to imine and azo group (3H), the latter is assigned to the protons ortho to hydroxyl groups (4H).

Table (1) : Physical Properties of the Synthesized Compounds II and IIIa-d

Compound No.	M.P ⁰ C	Yield%	Color
II	92-94	60	Orange
IIIa	173-175	73	Brown
IIIb	162-164	75	Orange
IIIc	166-168	80	Brown
IIId	158-160	82	yellow

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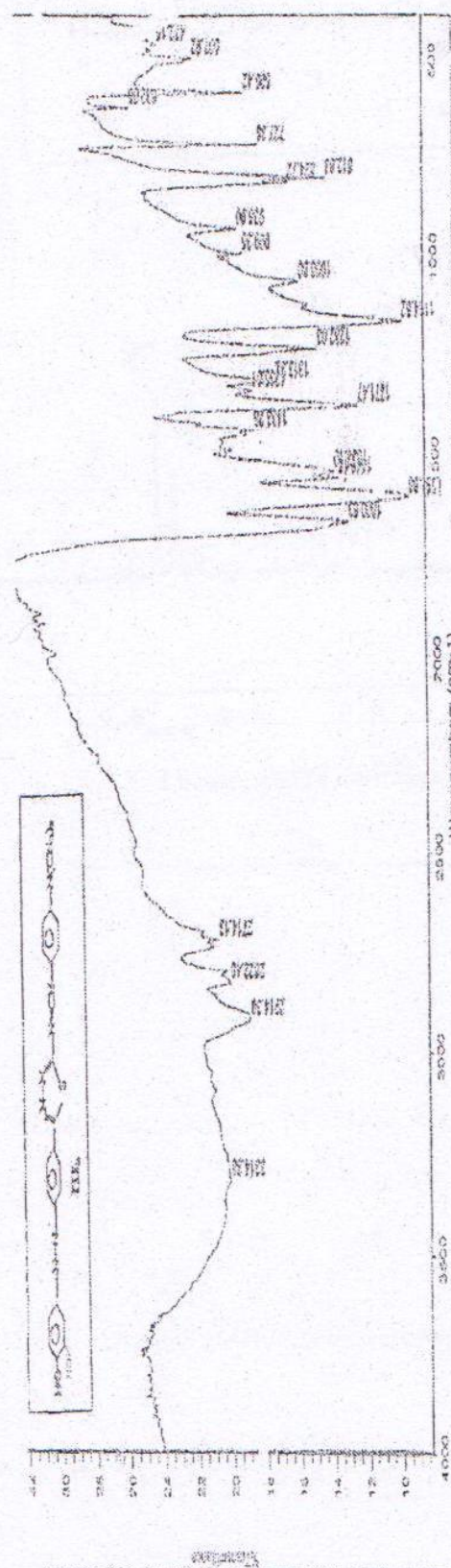
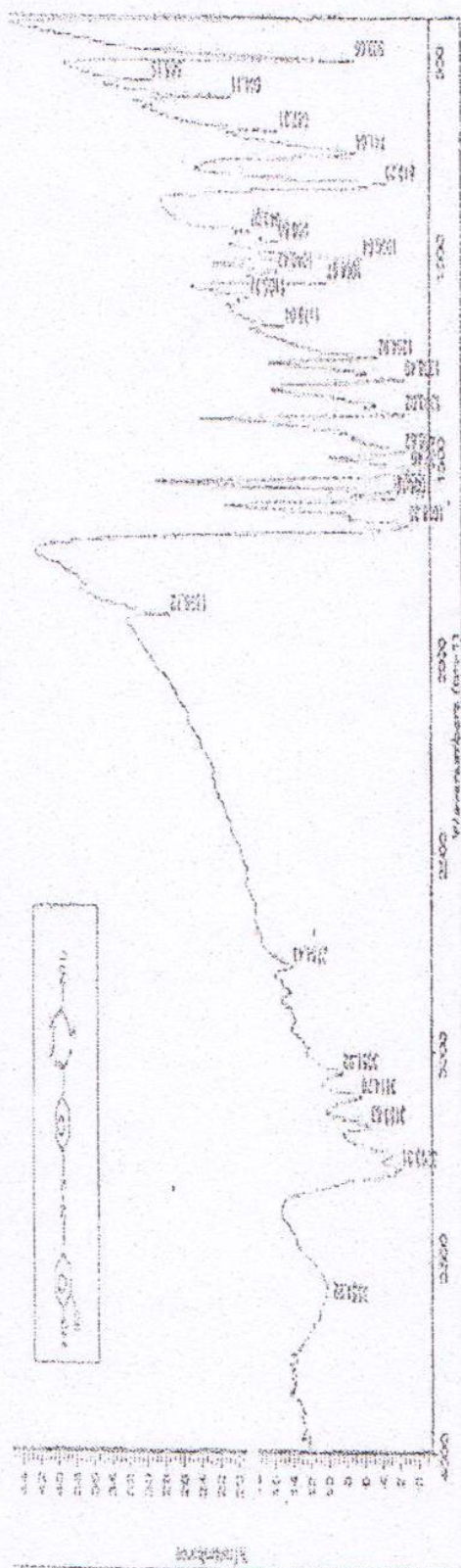
تحضير وتشخيص بعض معوضات ٤, ٣, ١- ثياديازول ومشتقاتها الجديدة

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الخلاصة

تم تحضير ٢-امينو -٥- (٤, ٣) ثنائي هيدروكسي فنيـل -ازو- بنزين (٤, ٣, ١) - ثياديازول وبعض معوضات بنزلدين امينو-٥-(٤, ٣)-ثياديازول شخـصت هذه المركبات بأستخدام مطيافية لاشعة تحت الحمراء والرنين النووي المغناطيسي للبروتون.



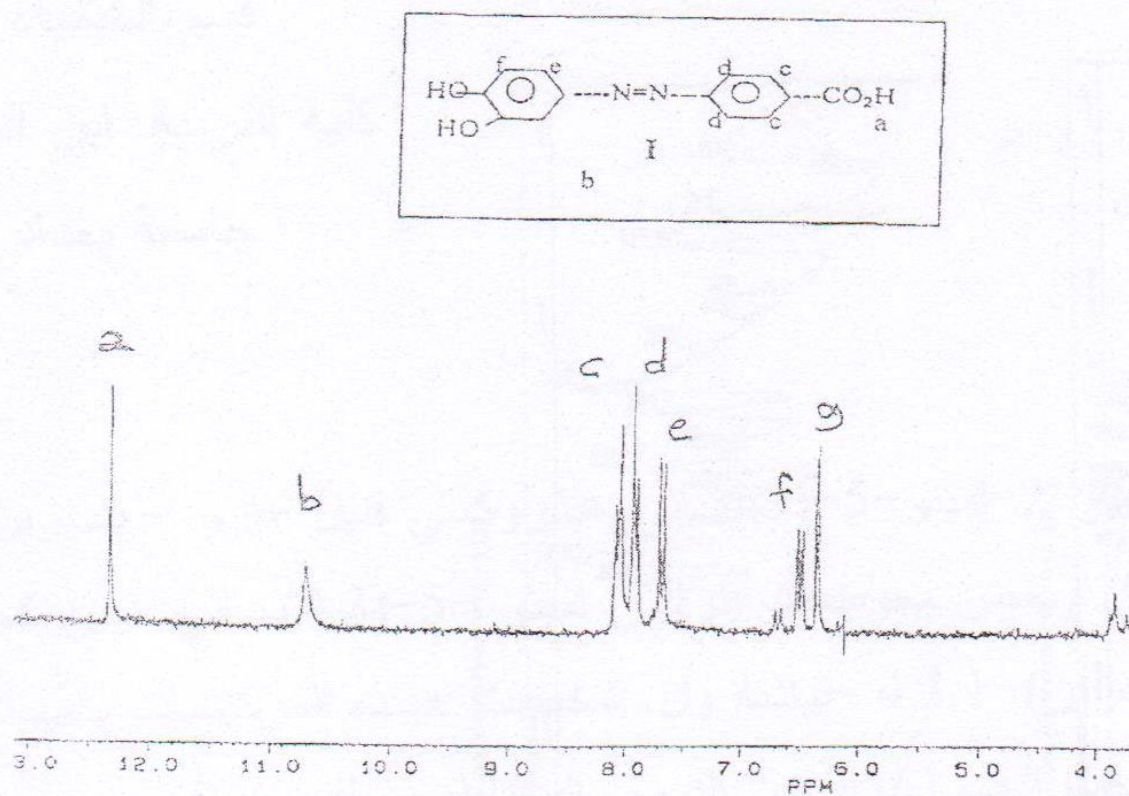


Figure 3 ¹H NMR spectrum of compound I

