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

Dr.ali h.samir
Chemistry Department
College of Education
Baghdad University

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

l-introduction :

l,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).ln addition many derivatives of aniline that had been used as dyes(6).
In this work 2-amino-5-(3,4-dihydroxy phenyl-azobenzene)-l,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 :

l-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 (l) : 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

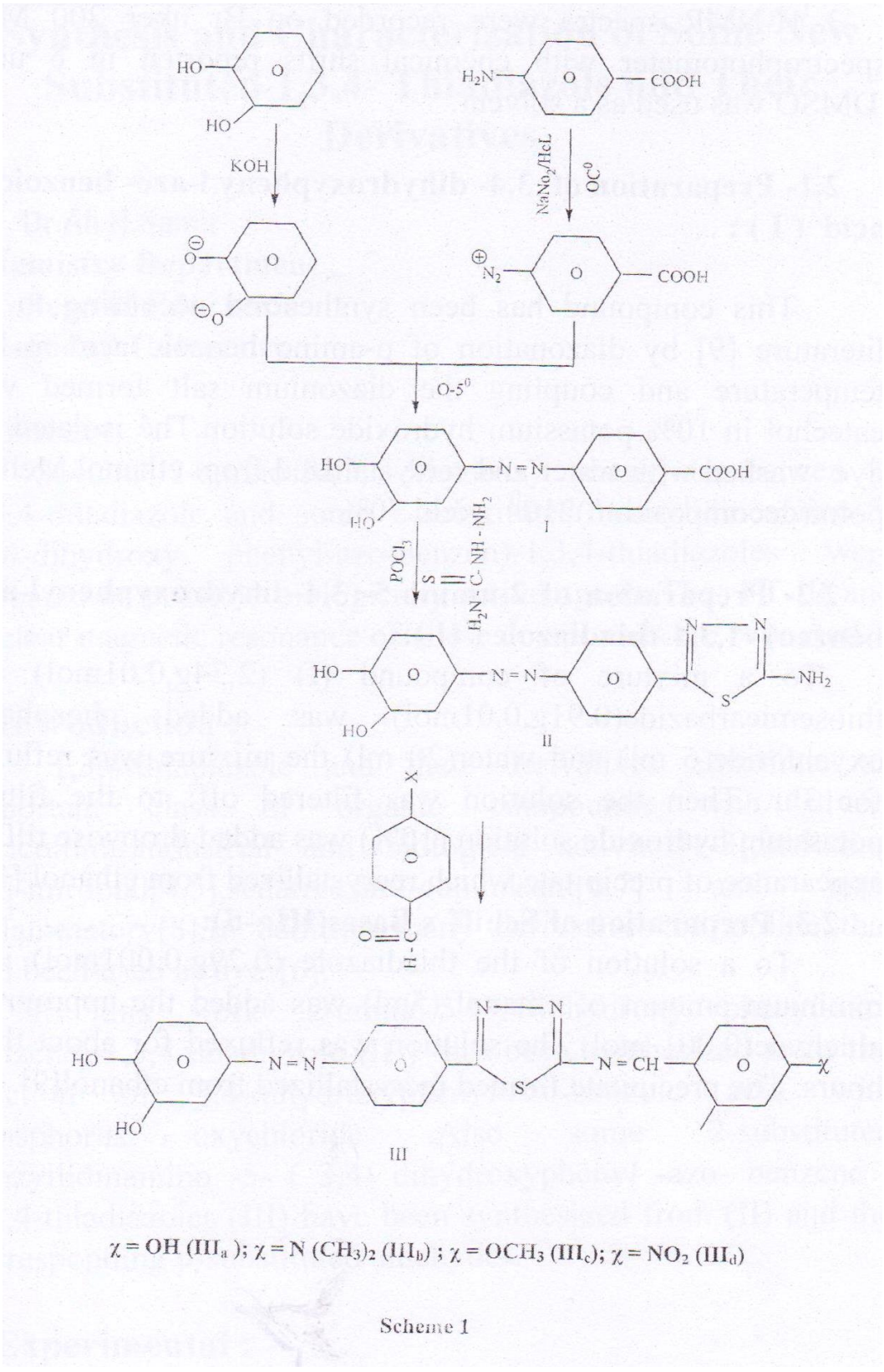
pointtdecomposition)210o; yield70%

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

To a mixture of compound (1) (2.34g,0.01mo1) and thiosemicarbazide(o.9lg,o.olmol) 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).



Scheme 1

3-Results & Discussion:

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

Il,1l1a-d are summarized in table 1 .

3.1- FT-IR Spectra (11-13) :
FT- IR spectrum (cm^{-1} potash ium 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 at3293cm^{-1} doublet) and at 1604 cm-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 assigned to CS stretching .other bands bing at 3105 3052 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 cm^{-1} ass assigned N=N and C=C (aromatic) stretching ;at 1393,1308,1254 cm^{-1} assigned to CN stretching and CO stretching.

2- The FT- IR spectrum of compound lllb(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 at2714cm-1assigned to N-CH_3stretching (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 bandstop 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 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- ^{1}HNMR Spectra [11 13] ^{1}HNMR spectrum (δppm,DMSO-d_6) :
1-^{1}HNMR 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 double at 8.07 (2H)with j_1=6 Hz and a doublet at 7.9 (2H)with j_l=6Hz.Therefore j_l is the coupling between the vicinal protons c,d.Doublet at 7.68 with j_2=8 Hz; a doublet -doublet at 6.5 (1H)with j_2=8Hz and j_3=3Hz.-Therefore j2 is the coupling between the vaginal protons e,f, and J3 is the coupling between the meta protons f. and g.

1HNMR spectrum of compound IIIa (figure 5)shows a
2-The singlet at 10.3 assigned to intramolecularely bonded OH proton (two broad signals of the same shape at 8.24 attributed to the vicinal aromatic(1H) of the middle ringt 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 groupt3H) ,the later is assigned to the protons ortho to hydroxyl groups(4h) .

Table (1) : Physical Properties of the Synthesized Compounds IIand 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 1,3,4- ثياديازول ومشتقاتها الجديدة

د.علي حمادي سمير

قسم الكيمياء –كلية التربية –ابن الهيثم-جامعة بغداد

الخلاصة

تم تحضير 2-امينو -5- (4,3 ثنائي هيدروكسي فنيل –ازو- بنزين)4,3,1 – ثياديازول وبعض معوضات بنزلدين امينو-5-(4,3-ثياديازول شخصت هذه المركبات بأستخدام مطيافية لاشعة تحت الحمراء والرنين النووي المغناطيسي للبروتون.

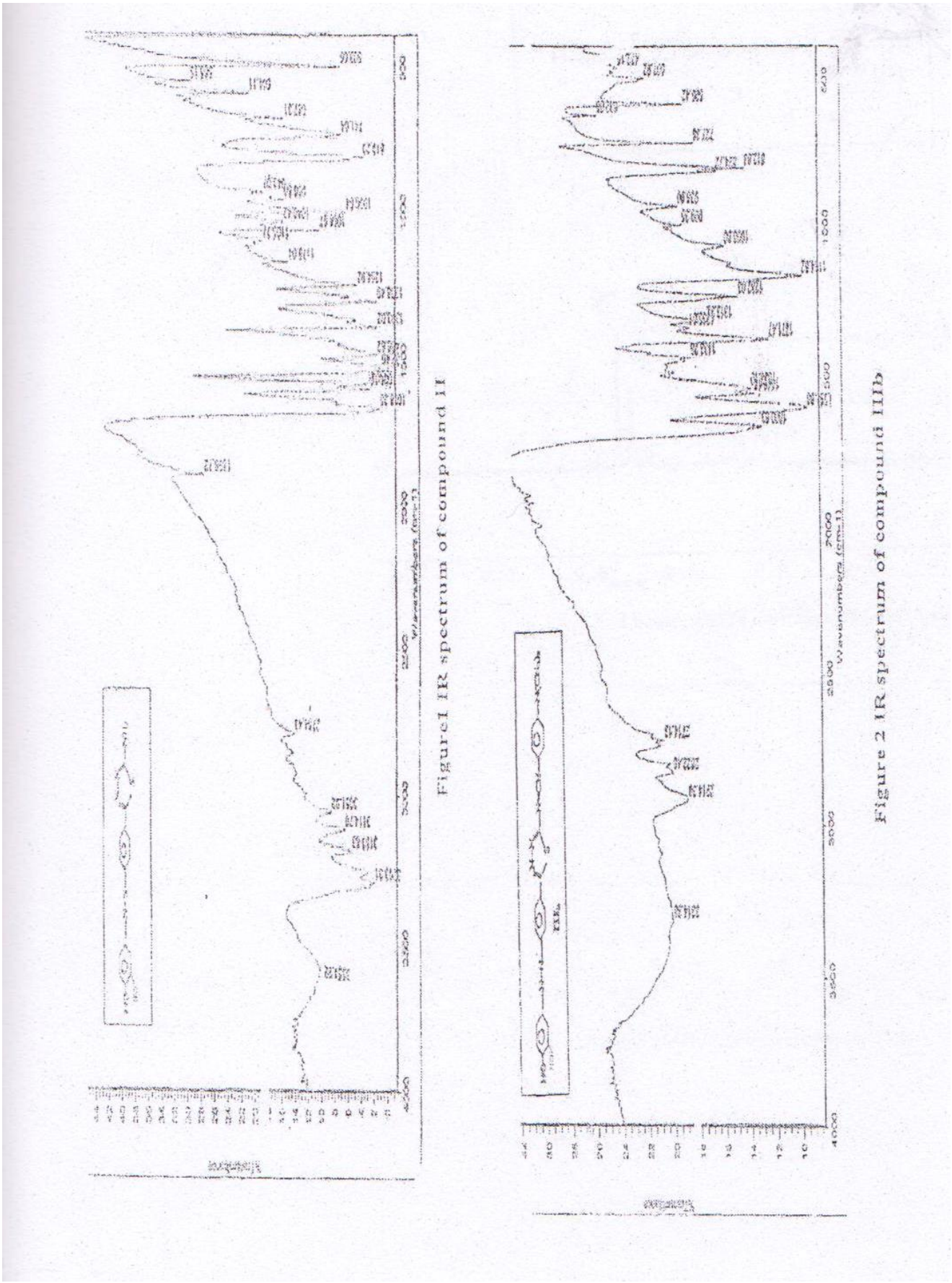

Figure1 IR spectrum of compound II

Figure 2 IR spectrum of compound IIIb