Synthesis of some new azo and shiff basederivatives derived from phthalazineandpyridazine

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Abstract :

The prepared compound 2-amino -5-mercapto -1,3,4-thiadiazol (1) was converted to hydrazineo derivative(2)by the reaction with hydrazine hydrate

Compound(2) was reacted with phthalic anhydride to give phthalazine derivative(3)and also maleic anhydride to give pyridazine derivative(4).

The amino group in these derivatives was converted to azo group (N=N) andazomethine (C=N)(shiffs base) .

Respectively using different aromatic phenol such as (resorcinol) and also different aromatic aldehydes such as (p- hydroxyl benzaldehyde , p- N,N-Di methyl benzaldehyde , p chlorobenzaldehyde).

The prepared compounds were identified using melting point apparatus , I.R- spectro photo meter and H^1-N.M.Rspectrophotometerfor compound (5,10,14).

Key words:.phthalazine,pyridazine, azo, shiff base derivatives .

Introduction :

Phthalazine compound like other member of the benzodiazine series has been widely applied as therapeutic agent due to its anticonvulsant ,cardiotonic ,vasorelaxant and antiinflammatory properties[(1)] Phthalazin e compounds have been prepared using gibbreal method[(2)]So many compounds can give these derivativese specially phthalicanhydride when

React with thionyl chloride and methanol The product of this step was allowed to react with hydrazine hydrate to give Phthalazin[(3)].

The compound 6,7-Diamino Phthalazine 1,4-(2H,3H)dione has been prepared and used as optical active agent [(4- 7)]

It is well known that pyridazines and related compounds possess important pharmacologicalactivity, mostof them related to the cardiovascular system[(8-9).]

(3,4,5-trimethoxy benzyl -6- methyl -3-chloropyridazinecompounds have been prepared using 4-(3,4,5 trimethoxybenzyl) -6-methyl – pyridazine -3- (2H)-one .

4-aryl -2,5-dioxo -8- phenyl pyrido (2,3-d) pyridazinederivatives have also been prepared using meldrum acid and X-Ray crystallography was used to identify the structures [(10-11).].

Experimental Part:

Melting point were determined using electro thermal melting point apparatus were(uncorrected) the I.R absorptronspectro were recorded by

F T I R model 84005 shimadzuJapanInfraedspectro photo meter as KBr disk .H1- N.M. R spectro were recorded by ultra shield 300 mHz .Bruker 2003.

2-1 :Synthesis of 2- amino -5- mercapto -1,3,4 thiadiazol (1) - The compound was prepared from thiosemicarbazid and carbon disulfide according to[(12)]previcone method.

.**2-2: Synthesis of 2- amino -5- hydrazine -1,3,4-thiadiazol (2)**hydrazine hydrate (0.02 mol),(0.00007g) was added to solution of 2-amino-5-mercapto-1,3,4- thiadiazol (1) (0.01 mol) in absolute ethanol (15ml)and the resulting mixture was refluxed for 6 hours[(13)]The solid compound separated on cooling was filtered off and dried .**2-3:. Synthesis of 2- amino -5-(1,2-dihydro phthalazine -3,6- dione -1-yl) -1,3,4thiadiazol (3)**equimoloar amount of 2-amino -5- hydrazine -1,3,4 –thiadiazol (2) (0.015mole), (0.00005g) and phthalic anhydride (0.015 mole)were dissolved in acetic acid (30 ml) and left under reflux for 10 hour .

then the reaction mixture was poured on crushed icd ,the formed crystal was collected by filtration .,air dried and recrystallized from chlorofrom The same method was used for maleic

anhydride to compound [(11)]

2-4:. Synthesis of diazonium salt of phthalazine and pyridazine (4) (0.01 mole), (0.00003g) of compound (3) or compound (11) was treat with (0.01mole) of sodium nitrite in hydro chloric acid (1.5ml) at 0-5 C

2-5 :. Synthesis ofazo compounds for phthalazine and pyridazine (5-7) ,(13-15) was reacted and allowed to react with pa (0.01 mole), (0.00003g)of substituted of phenol dissolved in 25 ml .of 12 % NaOHon cooling the solution of compound (4) or compound (12) added dropwise using ice bath with continous stirring . The preciptates was filtered ,washed with water and recrystallized from ethanol .

2-6 :. Synthesis ofshiffbase (8-10) and (16-18)equimolar amounts of compounds (3) or (11) (0.01 mole) , (0.00003g) and the s .ubstitutedaromatic aldehyde (0.01 mole) in absolute ethanol (25 ml.) were refluxed for 5hours . on cooling aprecipitatesobtained was filtered off ,washed with water ,dried and recrystallize from ethanol .

Table (1) : Physical properties of prepared compounds (1-9)

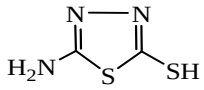
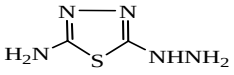
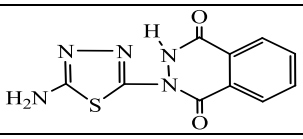
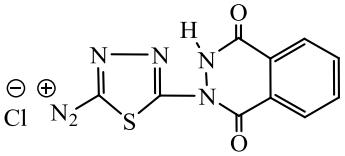
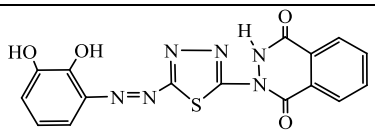
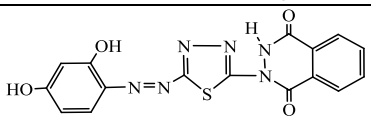
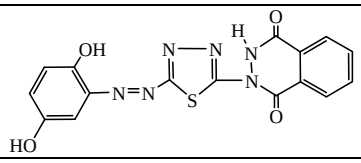
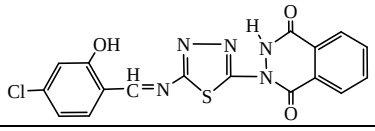
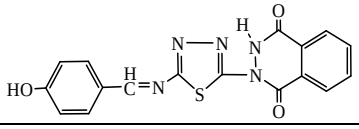
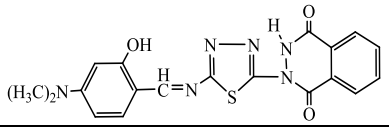
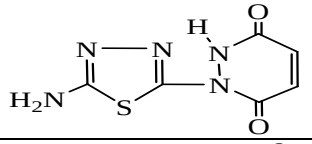
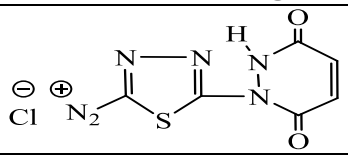
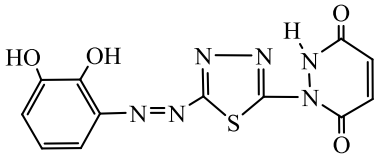
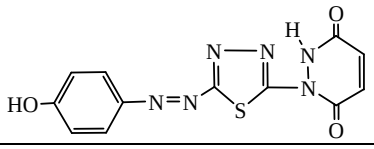
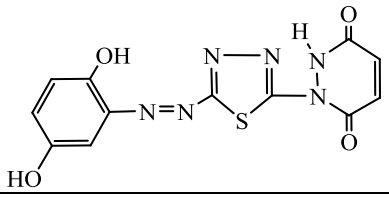
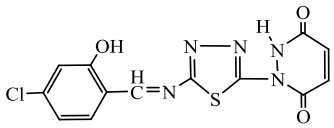
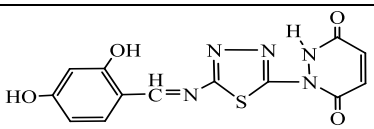
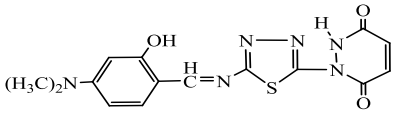
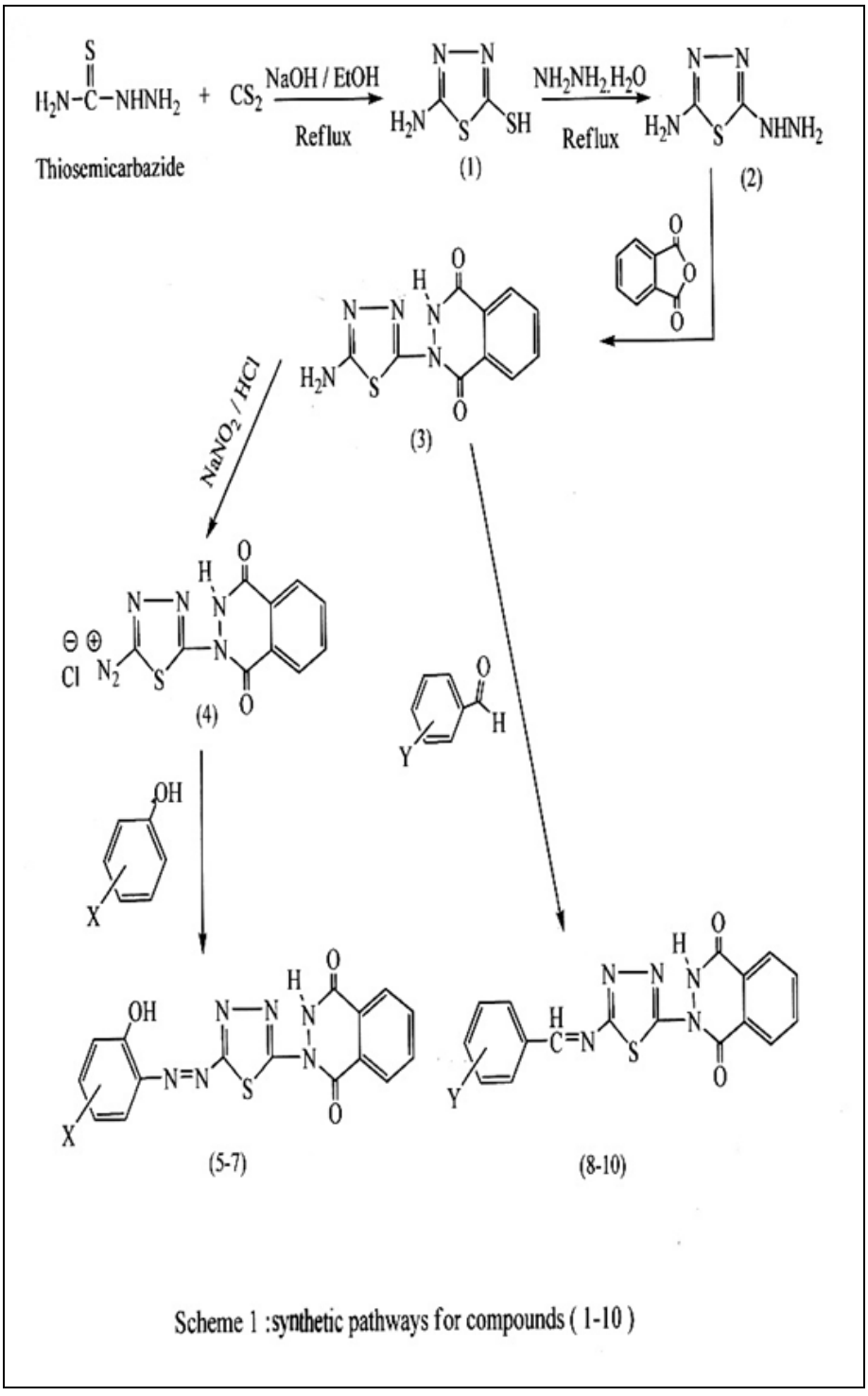
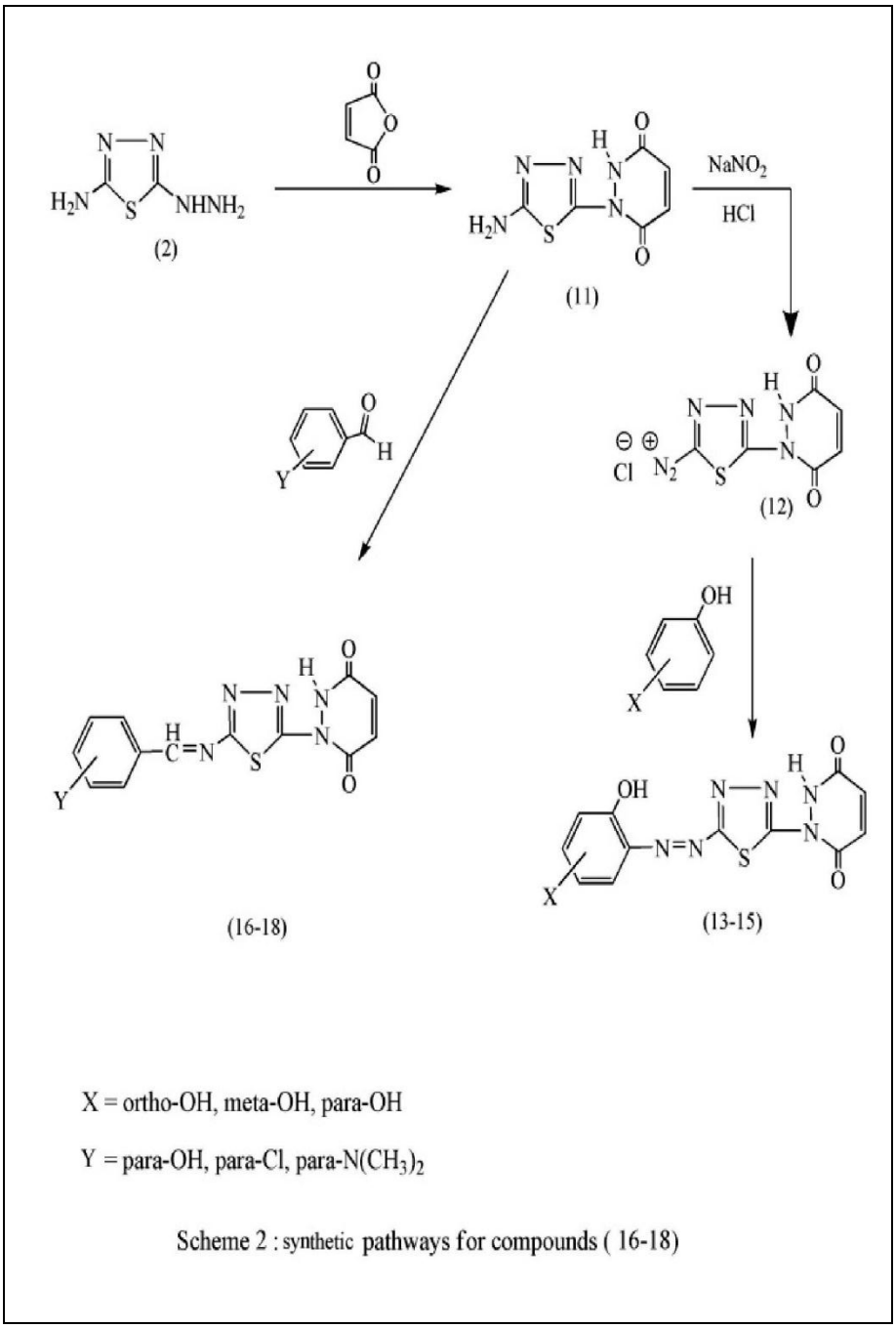
Comp. No.	Chemical structure	m.p °C	Yield %	Color	Name of Compound
1		225-227	75	White	**5-amino-1,3,4-thiadiazole-2-thiol**
2		242-244	68	White	**5-hydrazinyl-1,3,4-thiadiazol-2-amine**
3		198-200	77	White	**2-(5-amino-1,3,4-thiadiazol-2-yl)-2,3-dihydrophthalazine-1,4-dione**
4		-------	55	Yellow	**2-(1,3,4-thiadiazol)-5- (1,2-di hydro phthalazine 3,6-dione) diazonium chloride**
5		192-194	53	Yellow	**2-(5-(2,3-dihydroxybenzylideneamino)-1,3,4-thiadiazol-2-yl)-2,3-dihydrophthalazine-1,4-dione**
6		145-147	63	Grey	**2-(5-(2,4-dihydroxybenzylideneamino)-1,3,4-thiadiazol-2-yl)-2,3-dihydrophthalazine-1,4-dione**
7		132-134	65	White	**2-(5-(2,5-dihydroxybenzylideneamino)-1,3,4-thiadiazol-2-yl)-2,3-dihydrophthalazine-1,4-dione**
8		180-182	65	Grey	**2-(5-(4-chloro-2-hydroxybenzylideneamino)-1,3,4-thiadiazol-2-yl)-2,3-dihydrophthalazine-1,4-dione**
9		168-170	52	Yellow	**2-(5-(4-hydroxybenzylideneamino)-1,3,4-thiadiazol-2-yl)-2,3-dihydrophthalazine-1,4-dione**

Table (1) : Physical properties of prepared compounds (10- 18)

Comp. No.	Chemical structure	m.p °C	Yield %	Color	**Compounds names**
10		156-158	57	White	**2-(5-(4-(dimethylamino)-2-hydroxybenzylideneamino)-1,3,4-thiadiazol-2-yl)-2,3-dihydrophthalazine-1,4-dione**
11		185-187	63	White	**1-(5-amino-1,3,4-thiadiazol-2-yl)-1,2-dihydropyridazine-3,6-dione**
12		-----	58	Yellow	**2-(1,3,4-thiadiazoly)-5-1,2-dihydro pyridazine-3,6-dion) diazonium chloride**
13		135-137	61	Grey	**1-(5-(2,3-dihydroxybenzylideneamino)-1,3,4-thiadiazol-2-yl)-1,2-dihydropyridazine-3,6-dione**
14		181-183	56	White	**1-(5-(3-hydroxybenzylideneamino)-1,3,4-thiadiazol-2-yl)-1,2-dihydropyridazine-3,6-dione**
15		122-124	55	Yellow	**1-(5-(2,5-dihydroxybenzylideneamino)-1,3,4-thiadiazol-2-yl)-1,2-dihydropyridazine-3,6-dione**
16		210-212	52	Grey	**1-(5-(4-chloro-2-hydroxybenzylideneamino)-1,3,4-thiadiazol-2-yl)-1,2-dihydropyridazine-3,6-dione**
17		240-242	58	Yellow	**1-(5-(2,4-dihydroxybenzylideneamino)-1,3,4-thiadiazol-2-yl)-1,2-dihydropyridazine-3,6-dione**
18		155-157	60	White	**1-(5-(4-(dimethylamino)-2-hydroxybenzylideneamino)-1,3,4-thiadiazol-2-yl)-1,2-dihydropyridazine-3,6-dione**



Scheme 1 :synthetic pathways for compounds (1-10)



Scheme 2 : synthetic pathways for compounds (16-18)

Resuits and discussion :

The thiol group in 2- amino -5- mercapto -1,3,4,- thiadiazol (1) was converted into hydrazine derivative (2) by heating under reflux with an ethanolicsoiution of hydrazine hydrate.

The later compound was allowed to react with phthalic anhydride and maleic anhydride to synthesize phthalazine (3) and pyridazine (11) respectively The amino group in these compound was converted to azogroup and azomethine of diazonium salts by the reaction with different phenols and aromatic aldehydes respectively.

I.R spectra showed ($NHNH_2$) band for compound (2) absorbedat(3390-2230) cm^{-1} , (NH_2) band absorbedat ($3200cm^{-1}$) , (C=N) at 1610 cm-1 .

I.R spectraalso showed that the($NHNH_2$) band absorbedat (3300-3195)cm^{-1} for compound (3).

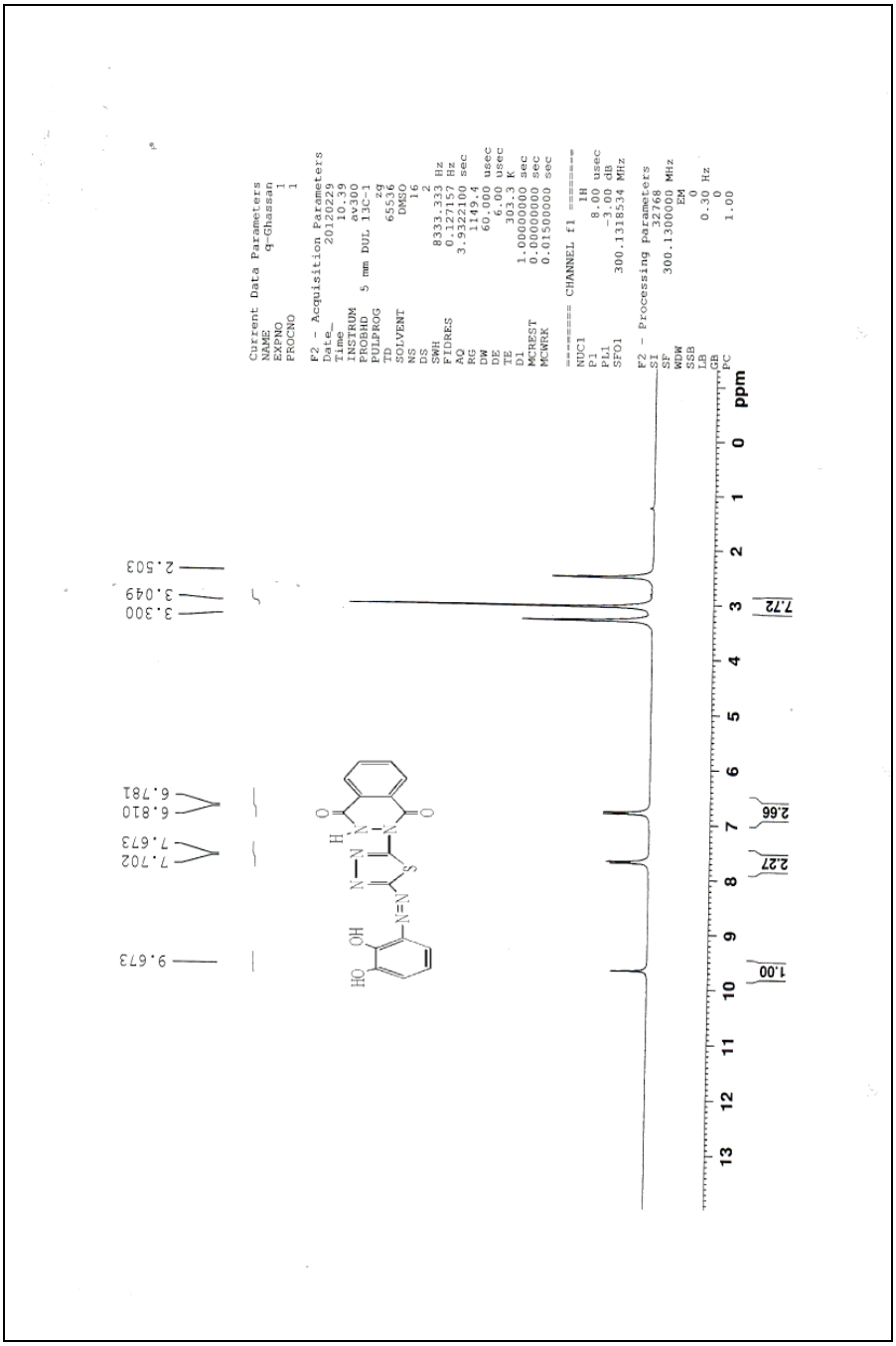
(C-H aromatic) absorbedat 3075 cm-1 and (C=O) at (1700) cm-1 for compounds (8-18)

I.R spectra also showed that (aromatic C- H) at 3100 cm-1 and . (C=N) at 1625 cm-1.

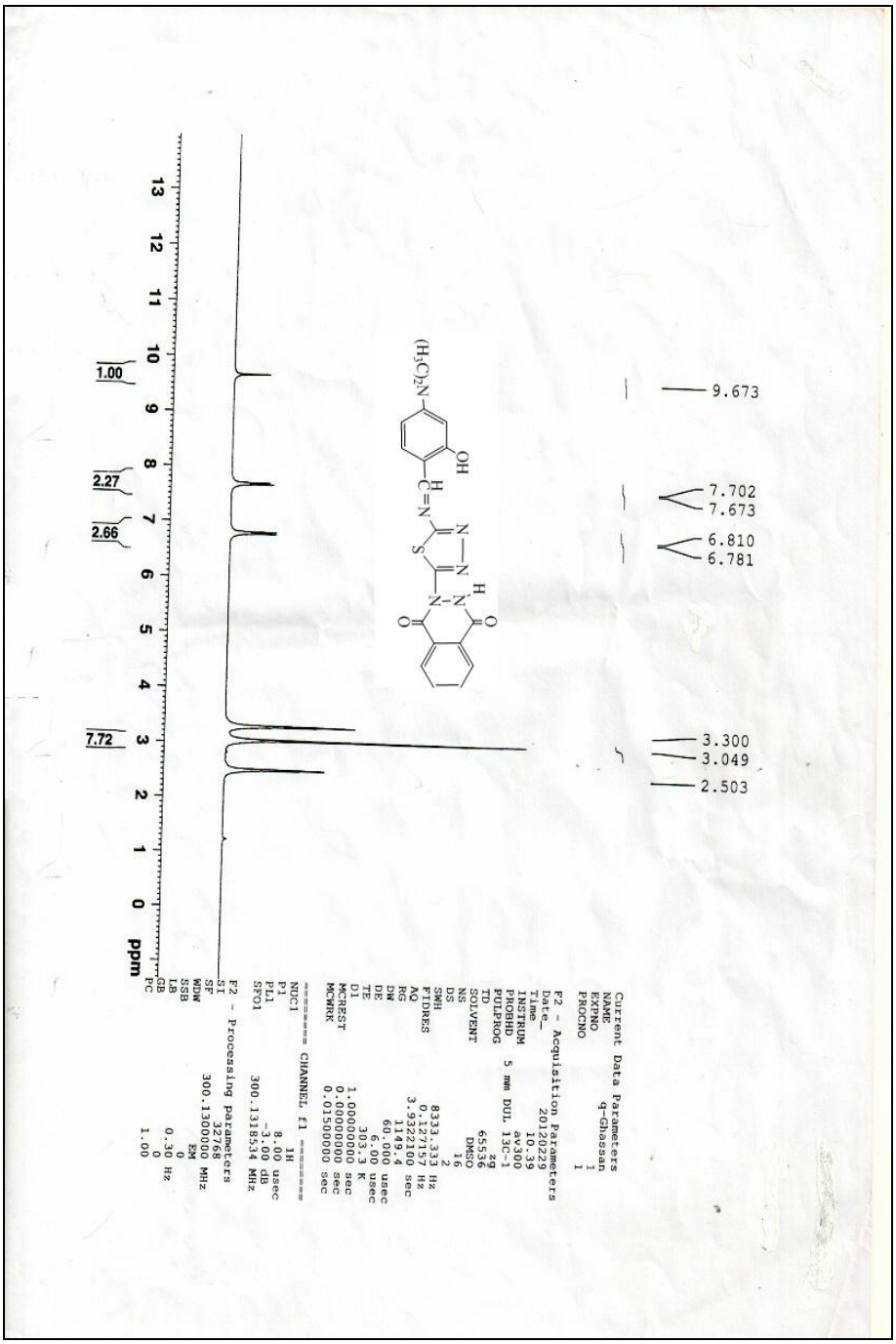
H^1-N.M.R data for compound (5) showed that benzene protons ring at (6.9-7.8) ppm and (9.8-10.5)ppm for OH and N-H . compound (10) showed signals resonating at (2.5-3.5) ppm for $(-NCH3)_2$ and (CH=N-) the protons ring at (7.6-7.7) ppm . compound (14) in the area (2.5) ppm , (7.1-7.5) ppm for protons of benzec and (10) ppm for (OH) . The figures (1-3) showedthe assigned.

Table (2)resuitobsorption data of I.R spectra and H: N.M:R data

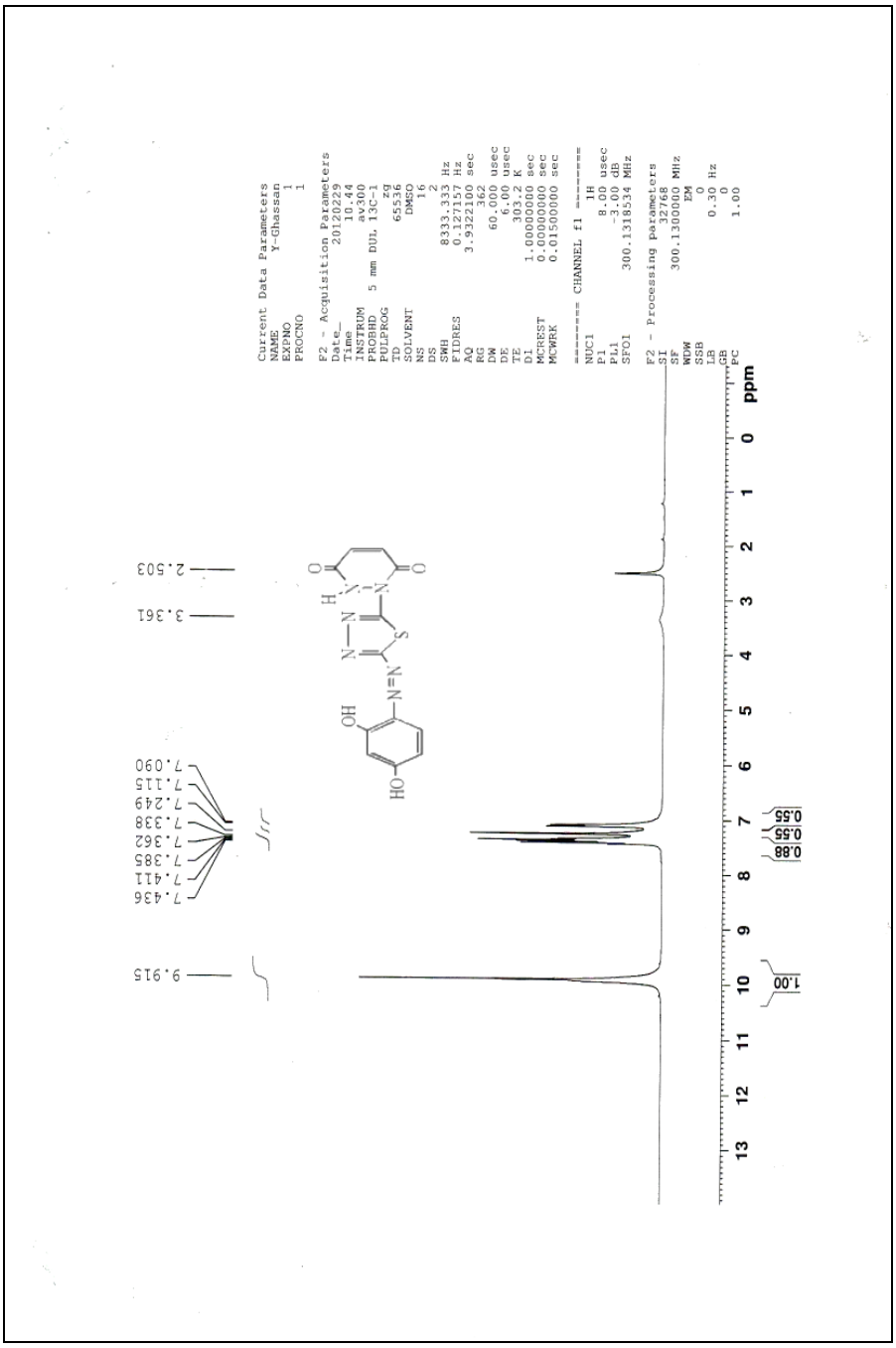
I.Rspectr data cm			H^1 -N.M.R		
Comp.No	νC-H Ar	νC=O	υC=N	OH	N(CH3)2
[2]	3075	1700	1610		
[5]				9.8-10.5	
[10]					2.5-3.5



شكل رقم (1) يمثل طيف H^1.N.M.R للمركب رقم (5)



شكل رقم (2) يمثل طيف H^1.N.M.R للمركب رقم (10)



شكل رقم (3) يمثل طيف H^1.N.M.R للمركب رقم (14)

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تحضير مشتقات جديدة لمركبات آزو وقواعد شف المشتقة من الفثالازينوالبيريدازين

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الملخص :

تم تحويل المركب 2- امينو 5-مركابتو 4,3,1 – ثايادايازول (1) الى مشتق الهيدرازينو (2) وذلك بمفاعلتة معالهيدرازين المائي . المركب (2) تم مفاعلتة مع انهيدريد الفثاليك لتحضيرمشتق الفثالازين (3) وكذلك تم مفاعلتة مع انهيدريد الماليك لتحضير مشتق البيريدازين (11). تم تحويل مجموعة الامينفي هذة المشتقات الى مجاميع آزو (-N=N-) وكذلك مجموعة الازوميثين (قواعدشف) (-C=N-) على التوالي باستخدام فينولات معوضة (ريزوسينول ، ميتاهيدروكسي فينول ، باراهيدروكسي فينول) وكذلك الديهايدات اروماتية باراهيدروكسي بنزالديهايد، باراكلورو- بنزالديهايدوبارا- N,N ثنائي مثيل امينوبنزالديهايد) تم تشخيص المركبات المحضرة باستخدام جهاز قياس درجة الانصهار ومطيافية الاشعة تحت الحمراء ومطيافية الرنين النووي المغناطيسي البروتون لبعض المركبات (14,10,5) .