Synthesis Of New Azomethine Dyes

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Abstract: The research includes the preparation of new azoketimines dyes by means of the coupling reaction of the schiff bases with various phenolic compounds . The prepared derivatives were diagnosed using infrared techniques, NMR proton, ultraviolet-visible radiation and thin-layer chromotography.

Keywords : Schiff base, Azo dyes, Azomethine, Coupling reaction .

1 . Introduction

Schiff bases are a type of organic compounds that contain an imine group or a group called azomethane (-N = C=) [1,2] . Also called schiff bases derived from aldehydes condensation With primary amines with aldeimines [3] . In the so - called schiff bases derived from the condensation of ketones with Primary amines with ketimine[4] . The stability of schiff bases depends on the type of amine compound and type aldehyde or ketone used where the preparation schiff bases are prepared from aromatic ketone and aromatic amine . The most stable between the schiff bases and the reason for this is attributed to increased stability of the resonance [5].

Azomethin dyes are of great importance and widely used in the textile, paper industries , Colored reagents for food and cosmetics [6]. Azomethin compounds are also bioactive , It has been used as an antifungal agent for bacteria and fungi [7] Cancer and other [8]

2 . Materials and methods of work

All compounds were purified by recrystallization followed by thin layer chromatography and modern spectral techniques. As for melting points, it was measured using Staurat MP/MP3 , Infrared spectra recorded using spectroscopy (Shimadzu FT – IR 8400 S) With a potassium bromide tablet.

Absorption spectra for radiation (UV-Vis.) Were measured in ethanol using a spectrometer (Shimadzu UV-Vis. 1600) . The proton NMR spectrum was taken using a BRUKER (300 MH_Z) spectrometer using a solvent (DMSO-d6) with a TMS as a standard reference. Chromatography was measured using Silica Gel TLC plates 60 F_{254}Merk.

3 . Methods of preparation

3.1 The general way to prepare schiff base

In RBF (100 ml), put (0.02 ml) of aromatic ketone and add (25 ml) absolute ethanol and (5 drops) Acetic acid and then gradually added to it (0.04 m) of aromatic amine and soluble in (20 ml) absolute ethanol with stirring continuously reflux reaction mixture for (2 hours) , The reaction was followed by thin layer chromatography. After heating, the

reaction mixture was cooled, then precipitated, dried and then recrystallization using ethanol

3.2 .The general way to prepare azo dyes

Preparation of diazione salt solution

In beaker, prepare a solution consisting of 10 mL cooled water and 10 mL concentrated hydrochloric acid and with continuous stirring (0.02 mL) of the prepared schiff base in the first part (A) with cooling in the ice bath (0-5) C°, then add to it a coolant solution consisting of (0.02 mol) sodium nitrite .

In a second beaker and within the ice bath, a solution consisting of dissolving (0.02 mol) phenolic compound with (15 ml) sodium hydroxide solution (10%). After continuous stirring in the ice bath, add the diazonium salt solution and drops to the coupling solution. After the addition of the mixture, stir the reaction mixture for 15 minutes in the ice bath. The precipitate is washed with water and then recrystallization using ethanol [9-11].

4 . Results and Discussion

This research included two steps: The first step was to prepare a new imine base (A) by reacting the condensation between cyclic aromatic ketone and the 1,4- phenilene di amine compound (Diagram1). The second step involved the preparation of new azo - methine dyes by reacting the schiff base prepared by the first step using the azonation reaction with several phenolic compounds (Diagram1). Eight new azonation derivatives were obtained (C 1-8) .All physical properties of prepared derivatives in Table (1). Table (2) represents all the spectral properties of the prepared compounds. Table (3) represents the spectroscopy of NMR.

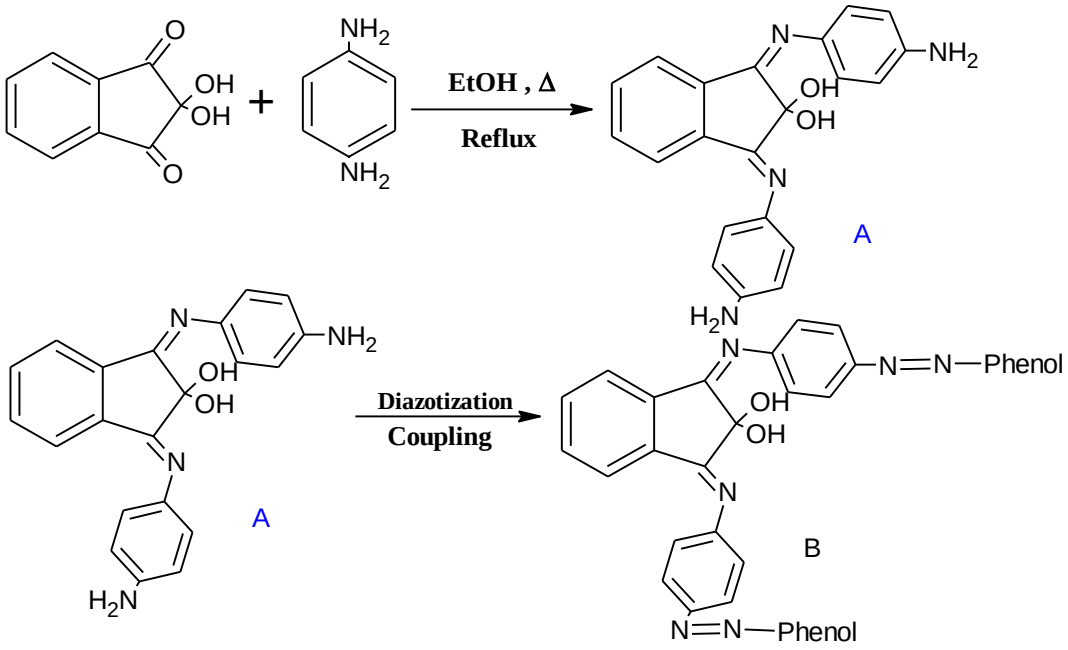

Diagram 1

Table (1) : Physical properties of prepared derivatives.

Com.	Phenol	M.Str.	M.wt. ($g.mol^{-1}$)	Yield (g , %)	M.P.(°C)	Color
A	-------	$C_{21}H_{18}N_4O_2$	358.39	(0.3 ,80)	182-180	D.Orang
1	phenol	$C_{33}H_{24}N_6O_4$	568.58	(0.4 , 60)	196-195	Yellow
2	1-Naphthol	$C_{41}H_{28}N_6O_4$	668.69	(0.5 ,70)	248-247	L. yello.
3	2-Naphthol	$C_{41}H_{28}N_6O_4$	668.69	(0.6 , 68)	262-261	Orange
4	Quinol	$C_{33}H_{24}N_6O_6$	600.58	(0.4 , 58)	223-222	Brown
5	Catechol	$C_{33}H_{24}N_6O_6$	600.58	(0.3 , 75)	211-210	L. Brow.
6	Resorcinol	$C_{33}H_{24}N_6O_6$	600.58	(0.4 , 65)	215-214	D.yello.
7	2-Amino phenol	$C_{33}H_{26}N_8O_4$	598.61	(0.3 , 55)	232-231	L.orang.
8	Thymol	$C_{41}H_{40}N_6O_4$	680.79	(0.2 , 50)	255-254	D.brow.

Table (2) : Spectral properties of prepared derivatives.

Com.	Phenol	λmax EtOH	FT-IR(cm^{-1}) KBr disk					
			- OH	CH_{ali} -*p*	-C=N	- N=N	-C–O	-OH ring
A	-------	-------	3429	-------	1635	-------	1284	-------
1	phenol	273	3420	-------	1631	1523	1290	1474
2	1-Naphthol	288	3418	-------	1614	1522	1294	1478
3	2-Naphthol	290	3419	-------	1618	1518	1293	1476
4	Quinol	275	3425	-------	1616	1522	1291	1475
5	Catechol	277	3427	-------	1625	1523	1292	1477
6	Resorcinol	275	3426	------	1617	1524	1294	1476
7	2-Amino phenol	295	3424	-------	1620	1526	1296	1480
8	Thymol	310	3422	2927	1623	1530	1298	1481

Table (3): Spectrometry (^{1}H-NMR) of prepared derivatives.

Comp.	Yield (g , %)	^{1}H-NMR (300MHz, DMSO-d_6, δ / ppm)
$C_{21}H_{18}N_4O_2$	(0.3 ,80%)	6.80(dd, 2H,J=1.14,8.42) ,6.60 (dd,2H,J=2.13,8,42) ,7.57 (ddd,6H,J=1.39,2.30,1.88) , 7.81 (dd,2H,J=7.58, 1.41 H_Z) , 7.88(dd,2H,J=1.41,7.58 H_Z)
$C_{33}H_{24}N_6O_4$	(0.4 , 60%)	6.99(dd , 2H , J=8.07 ,1.39 H_Z) ,7.44(ddd , 3H ,J= 3.03 ,1.77,7.25 H_Z) , 7.87(dd , 2H , J=1.37, 7.92 H_Z) ,7.91(dd , 2H ,J=1.39 , 8.07 H_Z) .
$C_{41}H_{28}N_6O_4$	(0.5 ,70%)	7.95(dd,1H,J=1.40,7.96 H_Z) , 7.41(ddd,2H,J=3.24, 1.82 5.94 H_Z) , 7.09(dd,1H,J=1.08,5.98 H_Z) , 7.85(dd,1H, J=8.56 H_Z) , 8.09(dd,1H,J=1.18,8.43 H_Z) , 8.03(ddd,1H, J=1.58,1.66,7.54 H_Z) .
$C_{33}H_{24}N_6O_6$	(0.4 , 58%)	7.86(dd,1H,J=7.79,1.39 H_Z) , 7.44 (ddd,2H,J=1.76, 2.26,7.32 H_Z) , 7.59 (ddd,2H,J=5.89,2.26,1.86 H_Z) , 7.17 (dd,1H,J=2.23,2.66 H_Z) , 7.08(dd,1H,J=2.66,8.53 H_Z) ,6.91(dd,1H,J=2.23,8.53 H_Z).
$C_{33}H_{26}N_8O_4$	(0.3 , 55%)	6.80 (dd,2H,J=1.14,8.42 H_Z) , 6.90(dd,2H,J=2.13,8.42 H_Z) , 7.18(dd,2H,J=2.13,1.14) , 7.57(ddd,6h,J=6.08,2.30,1.88 H_Z) ,7.81(dd,2H,J=7.58,1.41) .
$C_{41}H_{40}N_6O_4$	(0.2 , 50%)	1.18 (d,12H,J=6.93 H_Z) , 1.96(q,6H) , 3.23(ddd,2H,J=6.93 H_Z) , 6.99(d,2H,J=2.19 H_Z) , 7.40(ddd,4H,J=3.46,1.77,8.60 H_Z) , 7.44 (ddd,4H, J=8.60,3.19,1.93 H_Z) , 7.84,7.88 (dd,2H,J=1.40,7.59 H_Z) , 8.11 (d,2H,J=2.19 H_Z) .

The NMR spectrum of the azoketimines indicates that there are several overlapping electronic environments of the prepared compounds due to the diversity of the active groups found in these compounds in that they are driving or withdrawing aggregates (such as azomethine, hydroxyl, amine and alkyl groups), In addition to the abundance of hydrogen atoms and their diversity, which leads to the multiplicity of signals recorded spectrally and with frequent splitting , If we start with a compound (A), the signal value (6.60 ppm) refers to the adjacent protons of the base aromatic ring , The signal (6.80 ppm) belongs to the opposite protons of the aromatic amine compound, especially near the amine group . The opposite protons of the aromatic amine compound, close to the azomethin group, show a clear signal with double splitting (7.81 ppm) , As for the last value (7.88 ppm), it is due to the opposite protons of the basic aromatic ring, especially near the five rings. As for the phenol compound, one of the most significant signs of the characteristic resonance characteristic is the signal (6.99 ppm), which corresponds to the corresponding phenol ring protons, which are at the same time protons adjacent to the other phenol Leading to the double splitting And double . As for the pigment of the naphthol compounds, the most prominent signals measured are the values between the extended values (ppm 7.09 - 8.03) Which are related to the protons of the alpha-naphthol ring, which are close to the hydroxyl group and the withdrawing azo group , As well as the effect of the pi bonds of the aromatic ring on the environment of the emergence of hydrogen atom signals. As for azomethane dyes and prepared using phenol compounds hydroxyl The presence of groups (high electron density) creates electronic environments that obscure or reduce the appearance of signals and thus reduce their measured values or observation, This is observed for these compounds the most important of which are the measured values (7.17 – 6.91 ppm) which belong to the ring protons of (-OH) groups. The characteristic and phenolic value of the phenolic compound is a signal between (7.18 - 6.80 ppm), which comes from protons confined between the azo group and the amine and hydroxyl groups.

For the latter compound thymol there are several distinctive signs, the most important signal (3.23 ppm) Which is due to proton isopropyl group, which is affected by the high electronic environment of the two methyl relative groups , As well as the signal (1.96 ppm) for the three methyl group groups adjacent to thymol, Another characteristic signal is the six isopropyl protons, which have a value (ppm 1.18), and the signal of value (6.99 ppm) belongs to the proton and thymol ring between the two groups of methyl and hydroxyl.

6 . COSY spectra of prepared derivatives

It is a modern spectral method and represents the 2D NMR spectroscopy. This type of spectroscopy provides valuable information planned and plotted in the vacuum based on two frequencies rather than one frequency. (^{1} H -^{1} H) shift correlation they identify protons that are coupled (I,e. , that split each other's signal) .This is called shift – correlated spectroscopy , which is known by the acronym COSY. This is therefore very useful in determining the structure of the molecule better than the one dimensional spectroscopy. The figures (1–5) .

The spectrum of the cosy depends on its interpretation of the cross peaks, which are the peaks that form and represent the radius of the contour peak **,** It is this the contour peak that helps to identify and allocate the intersecting peaks of the protons of prepared compounds , , Even if we start with the prepared schiff base, the cosyi spectrum shows that the intersecting top node (1) belongs to the adjacent protons of the base aromatic ring , While protons peaks cross-numbered (2, 3) it signals the four protons of the ring opposite and adjacent aniline together , The group Alazumethein On the other hand , The recent summit of this derivative numbered (4) go back to the protons opposite ring aromatics base , As for the dye, the phenolic prepared the most prominent peaks are cross-dating back to the protons of the ring opposite phenolic as well as neighboring protons which represent the peaks of the cross (5,7).

The dye alpha - naphthol, it features a cross-peaks (9, 13) **,** which date back to the protons alpha - naphthol ring which are found close to or sandwiched between two groups of azo and hydroxyl for the peak (9), Or go back to the four protons opposite and adjacent to the ring for the foundation naphthol aromatics peak (13).

The spectrum of the aminophenol derivative is one of the most important intersecting peaks. It is the peak (14) which belongs to the protons of the aromatic ring of aminophenol, Also, the peaks (15 ,16**)** is also distinct and represents the protons of the aminophenol splitting , especially between the two groups of amine and Azo withdrawing , As well as the displacement caused by protons ring aromatics adjacent the base of the compound that gives cross the peaks numbered (17 ,18).

The thymol dye is one of the most important intersecting peaks, which is attributed to the protons of the isopropyl group numbered(19) As well as the special instance of a group Protons spectrum associated with the ring thymol numbered peak (20) . The numbered peak (21) is characterized by the proton isopropyl group, which is affected by the groups of the two-motile instance, which surrounds it , For proton, the thymol ring between the hydroxyl and methyl groups It gives a distinctive and numbered peak (22) [18-19].

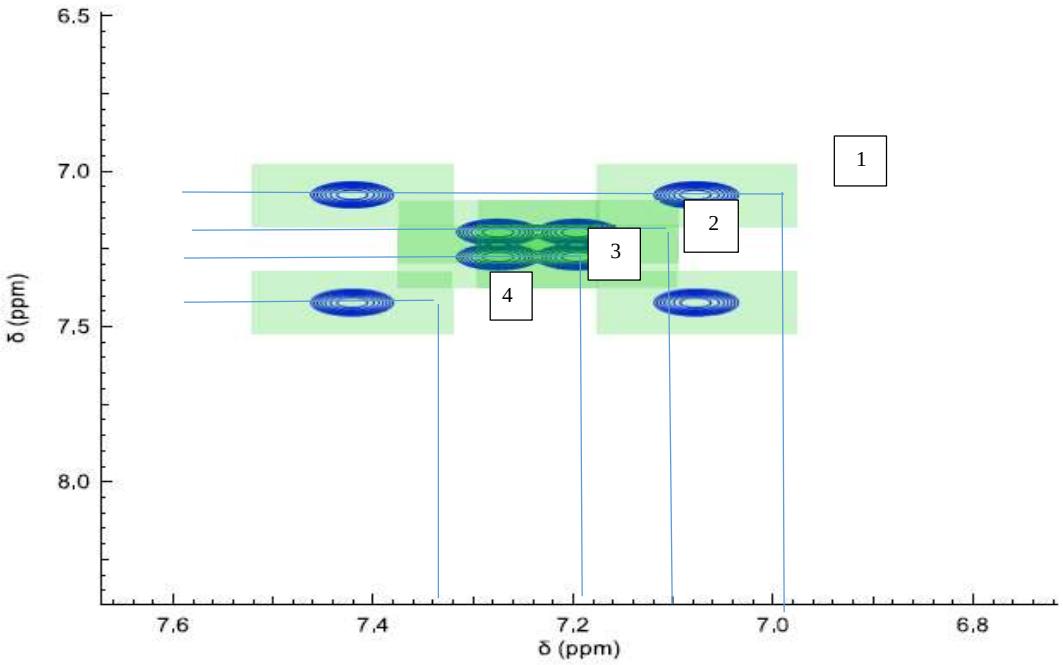

Fig. (1): COSY spectrum for prepared schiff base.

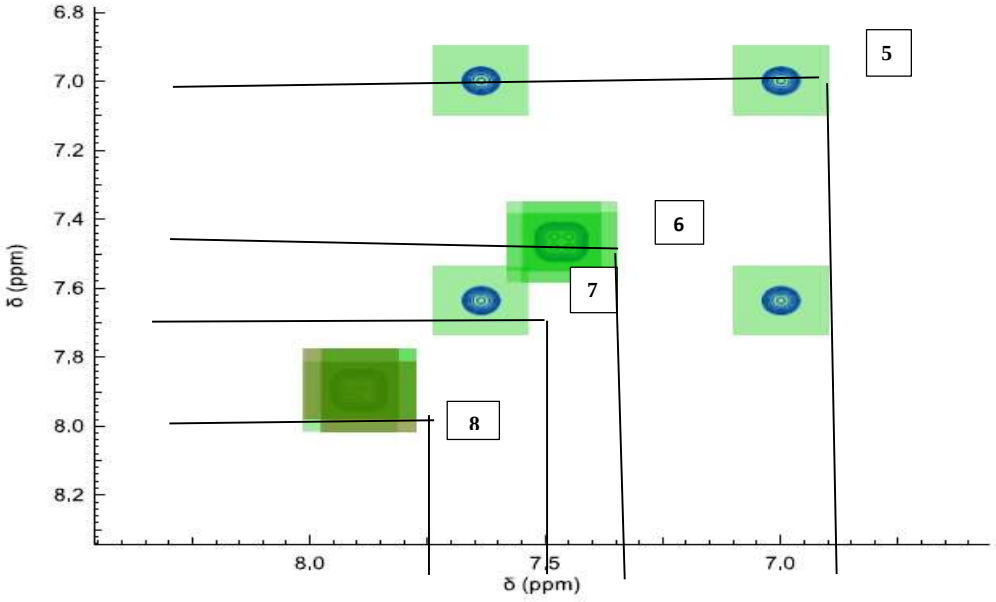

Fig. (2): COSY spectrum of the phenol derivative

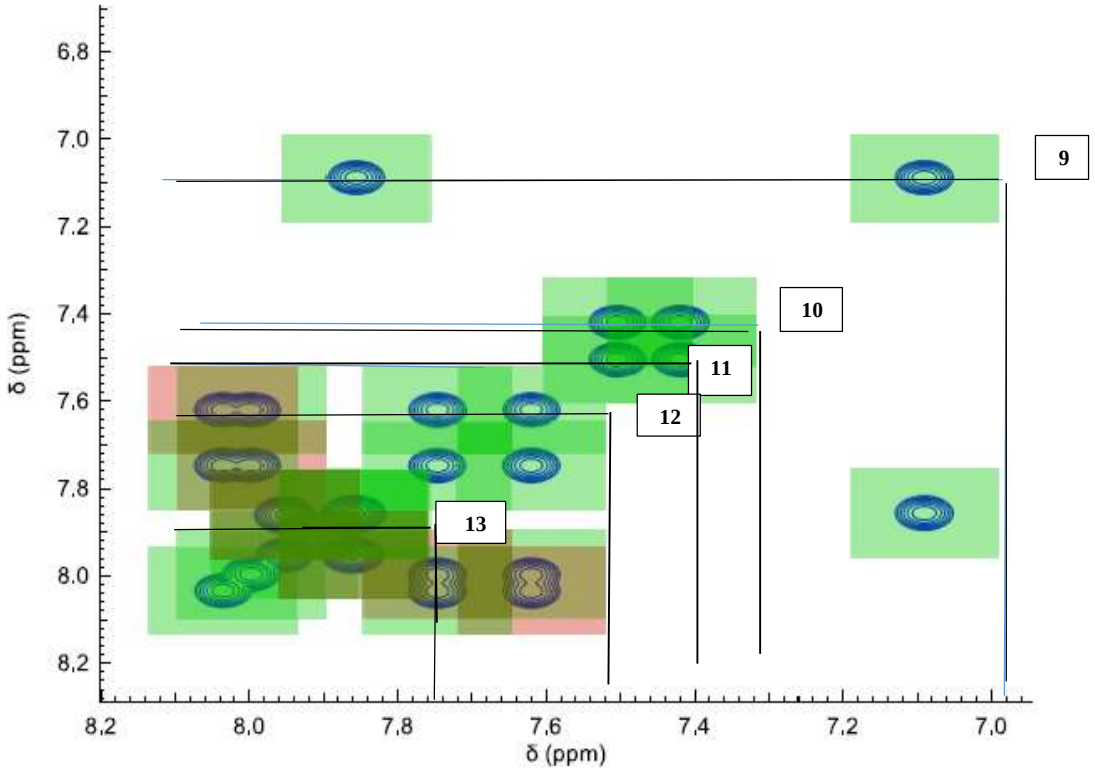

Fig. (3): COSY spectrum of the alpha-naphthol derivative.

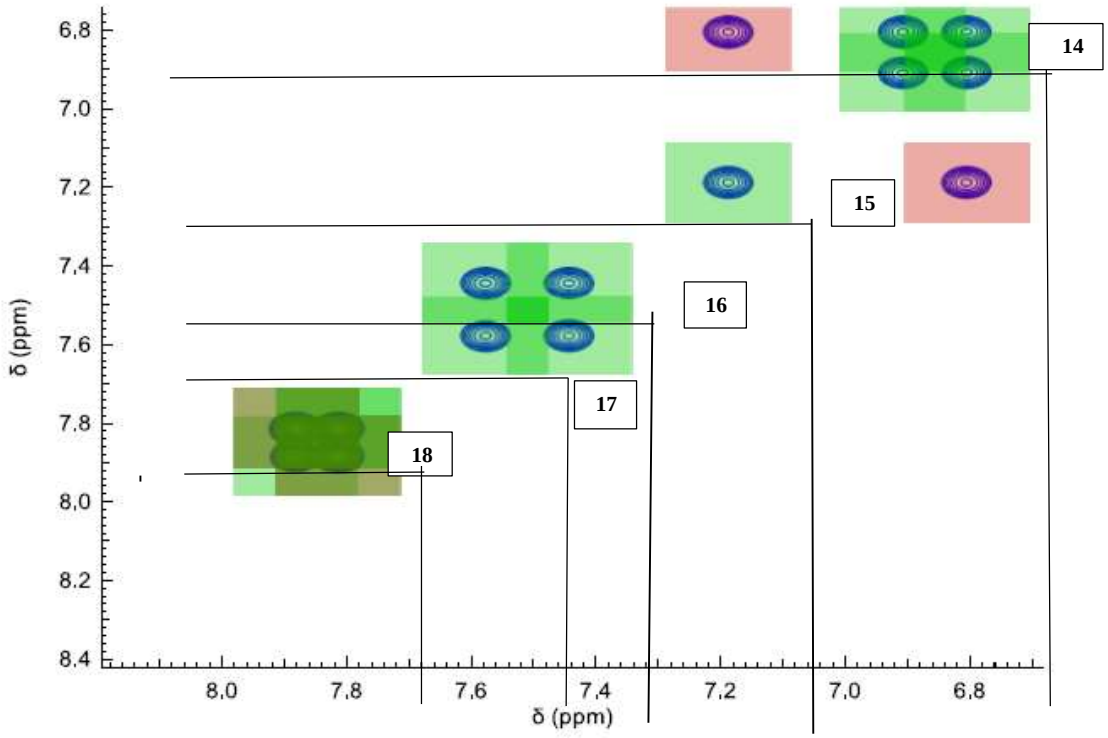

Fig. (4): COSY spectrum of aminophenol derivative.

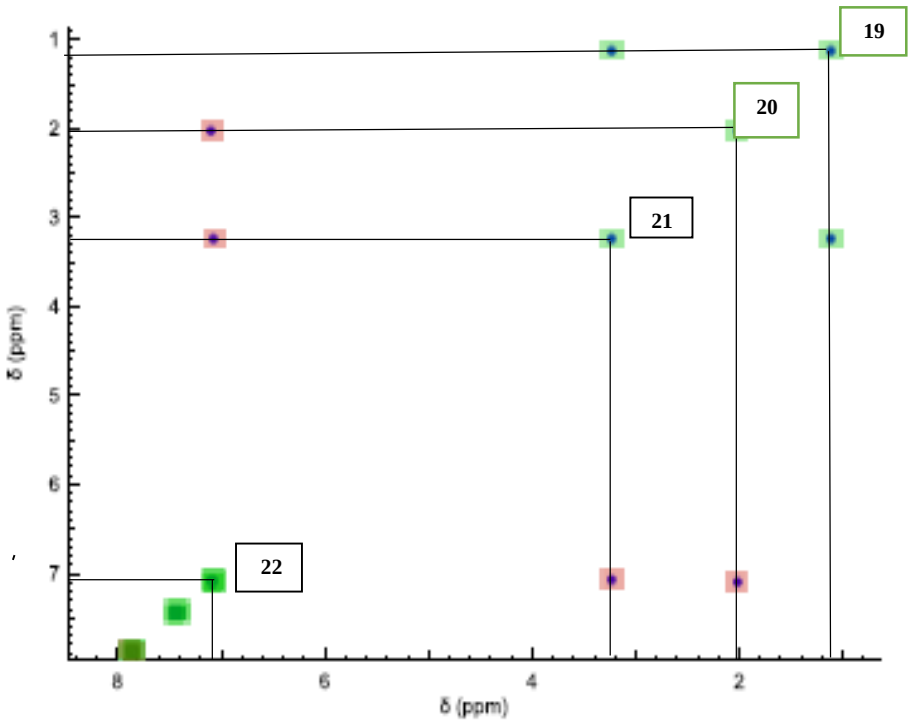

Fig. (5): COSY spectrum of the thymol derivative

7. Conclusion

The main objective of this research is to prepare new azo-ketimines containing several phenolic derivatives and using one of the important organic reactions, Which is the azotination reaction , Classical and modern techniques have been used in the diagnosis of composites such as melting points measurements , Use chromatography of thin film, infrared , UV - Visible, and Proton Spectroscopy NMR . COSY spectrum technology was also adopted for some of the main derivatives prepared .the percentages of derived derivatives ranged almost from average to good, In this research, we hope to develop new dyes of azoketimines that are used in some industrial and applied fields such as dyes, various medicines [12-14] , Cosmetics, colored reagents [15-17] , analytical chemistry guides and other such vital and industrially important fields[20].

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