Preparation and Characterization of Some New Azo Compounds Derived from Amino Pyrimidine

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Ekhlas Q. Jasem
Department of Pharmaceutical Chemistry, College of Pharmacy,
Basrah University, Basrah, Iraq
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Abstract

Four new azo compounds derived from amino pyrimidine and benzoic acid, salicylic acid, p-hydroxybenzoic acid and resorcenol were prepared. The characterization of the synthesized azo dyes has been described by IR and ^{1}H-NMR spectroscopic techniques.

Keywords: Azo dyes, amino pyrimidine, ^{1}H-NMR

1. Introduction

Azo compounds are highly colored and have been used as dyes and pigments for a long time. They have been receiving much attention and have been widely used in many practical applications such as coloring fibers [1,2], photoelectronic applications [3], printing systems [4,5], optical storage technology [6], textile dyes [7-9] as well as in many biological reactions [10, 11] and in analytical chemistry [12,13]. Recently, metal complex dyes have also attracted increasing attention due to their interesting electronic and geometrical features in connection with their application for molecular memory storages, nonlinear optical elements, printing system, etc [14, 15]. Therefore, several studies have been published on the synthesis and spectral properties of several azo barbiturates and aminoquinoline, as well as their transition metal complexes, so far [16].

In this work, four new azo compounds were synthesized from amino pyrimidine and some benzoic acid derivatives and phenolic compounds. The characterization of the azo compounds has been performed by melting points, IR and ^{1}H-NMR spectra.

2. Experimental

2.1 General

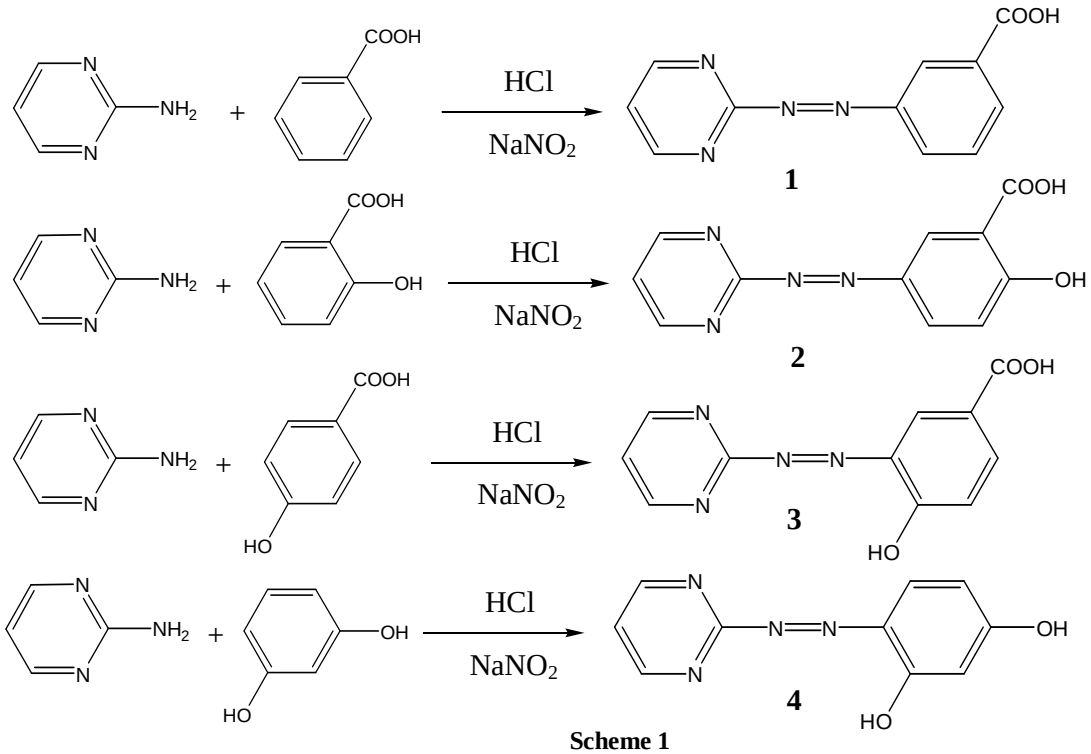
All the reagents and solvents were of reagent-grade quality and were purchased from Merck and Aldrich, and used without further purification for solid materials and with twice distillation for liquid materials. The uncorrected melting points were determined on a Gallenkamp Thermal Point Apparatus. Infrared spectra (in KBr pellets) were recorded on a FTIR 8400S SHIMADZU (Japan). The ^{1}H-NMR spectra in DMSO-d6 or $CDCl_3$ were measured at 300 MHz using Bruker AC 200 FT-NMR spectrometer using TMS as an internal reference.

2.2.1. Diazotization [17]

Amino pyrimidine (20 mmol, 0.19 g) was dissolved in 5 ml of 2 M HCl. The solution was then cooled to 0-5^o C in an ice-bath and maintained at this temperature. Sodium nitrite (20 mmol, 0.138 g) water (5 ml) solution was then added drop wise with continues stirring for 10 min at the same temperature.

2.2.2. General procedure for preparation of azo dyes [17]

The diazonium solution was added portion wise to the coupling component solution prepared by mixing a suspension of 1 mmol of benzoic acid (0.122 g), p-hydroxybenzoic acid (0.138 g), salicylic acid (0.138 g) and resorcenol (0.11 g) (Scheme 1) in 10 ml of water with sodium carbonate (3 mmol, 0.32 g) dissolved in 15 ml of water. During the procedure the pH value was maintained within 9-10 and the temperature at 0-5^{o} C. The mixture was stirred for 6 hrs, then the pH value was decreased to about 6. The mixture was kept overnight. The precipitated crude dyes were collected by filtration, washed with water, ethanol and acetone. Table 1 shows the characterizations of the prepared compounds.



Scheme 1

Table 1 :The characterizations of the compounds 1-4

Compound	Formula	Molecular weight	Yield (%)	mp (^{o}C)
1	$C_{11}H_8N_4O_2$	228.21	92	152-154
2	$C_{11}H_8N_4O_3$	244.21	89	147-150
3	$C_{11}H_8N_4O_3$	244.21	96	204-206
4	$C_{10}H_8N_4O_2$	216.20	96	Semi solid

3. Results and Discussion

3.1. IR spectra

The IR spectra for all azo compounds were performed by KBr disc method. Table 2 represents the data of the important bands of the IR spectra of the four prepared compounds.

All IR spectra of the compounds showed a broad band in the range 3675-3100 cm^{-1} which characteristic of O-H stretching vibration of hydroxyl of phenolic and carboxylic groups. First three compounds showed a strong band in the range 1701-1699 cm^{-1} attributed to C=O stretching of carboxyl group of acid moiety.

All prepared compounds showed a strong-medium bands in the ranges 1565-1540 cm^{-1} and at 1288-1230 cm^{-1} and 1190-1142 cm^{-1}, the first band is attributed to the N=N stretching vibration of azo group and the second bands are attributed to C-N and C-O stretching vibrations of the two fragments.

Table 2 :The important IR data of the compounds / cm^{-1}

Compound	O-H	C=O	N=N	C-N, C-O
1	3310	1699	1565	1288, 1182
2	3300-3100	1701	1540	1230, 1142
3	3613, 3320	1701	1554	1236, 1150
4	3675	-	1565	1288, 1190

3.2. ^{1}H-NMR spectra

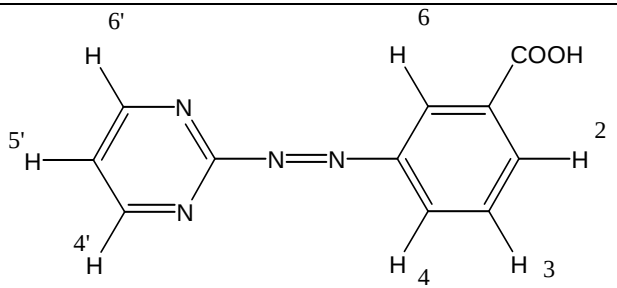
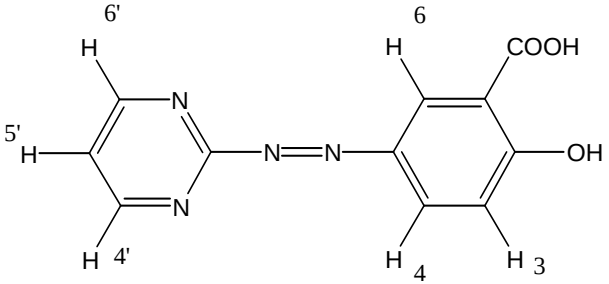
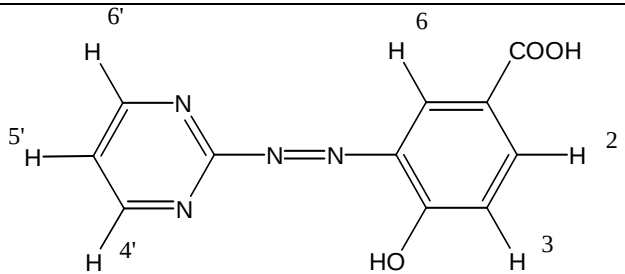
Figures 1-3 represent the ^{1}H-NMR spectra of the prepared compounds. These compounds exhibited multiplet signals due to aromatic proton systems and singlet signals due to characteristic hydroxyl groups.

All compounds showed multiplet signals at the range 7.504-8.156 ppm related to three protons of pyrimidine ring, as shown in Table 3.

All compounds exhibited downfield chemical shift singlet signals at the range 10.183-12.375 ppm due to the protons of carboxylic and phenolic groups.

The compound 1 showed multiplet signal between 7.463-7.651 ppm related to four protons of benzoic ring. Whereas, the compounds 2 and 3 showed multiplet signals at 6.918-7.036 ppm and 6.797-6.835 ppm, respectively, attributed to three protons of phenyl ring moiety, as shown in Table 3 and Figures 1-3.

Table 3: ^{1}H-NMR data of azo compounds in DMSO

Compound number	Compound	H-phenyl group	H-pyrimidine	COOH	OH
1		7.463-7.651 (m, 4H; H-2, H-3, H-4, H-6)	8.123-8.156 (m, 3H; H-4', H-5', H-6')	10.343 (s)	-
2		6.918-7.036 (m, 3H; H-3, H-4, H-6)	7.504-7.957 (m, 3H; H-4', H-5', H-6')	10.368 (s)	*
3		6.797-6.835 (m, 3H; H-2, H-3, H-6)	7.758-7.806 (m, 3H; H-4', H-5', H-6')	10.183 (s)	12.375 (s)

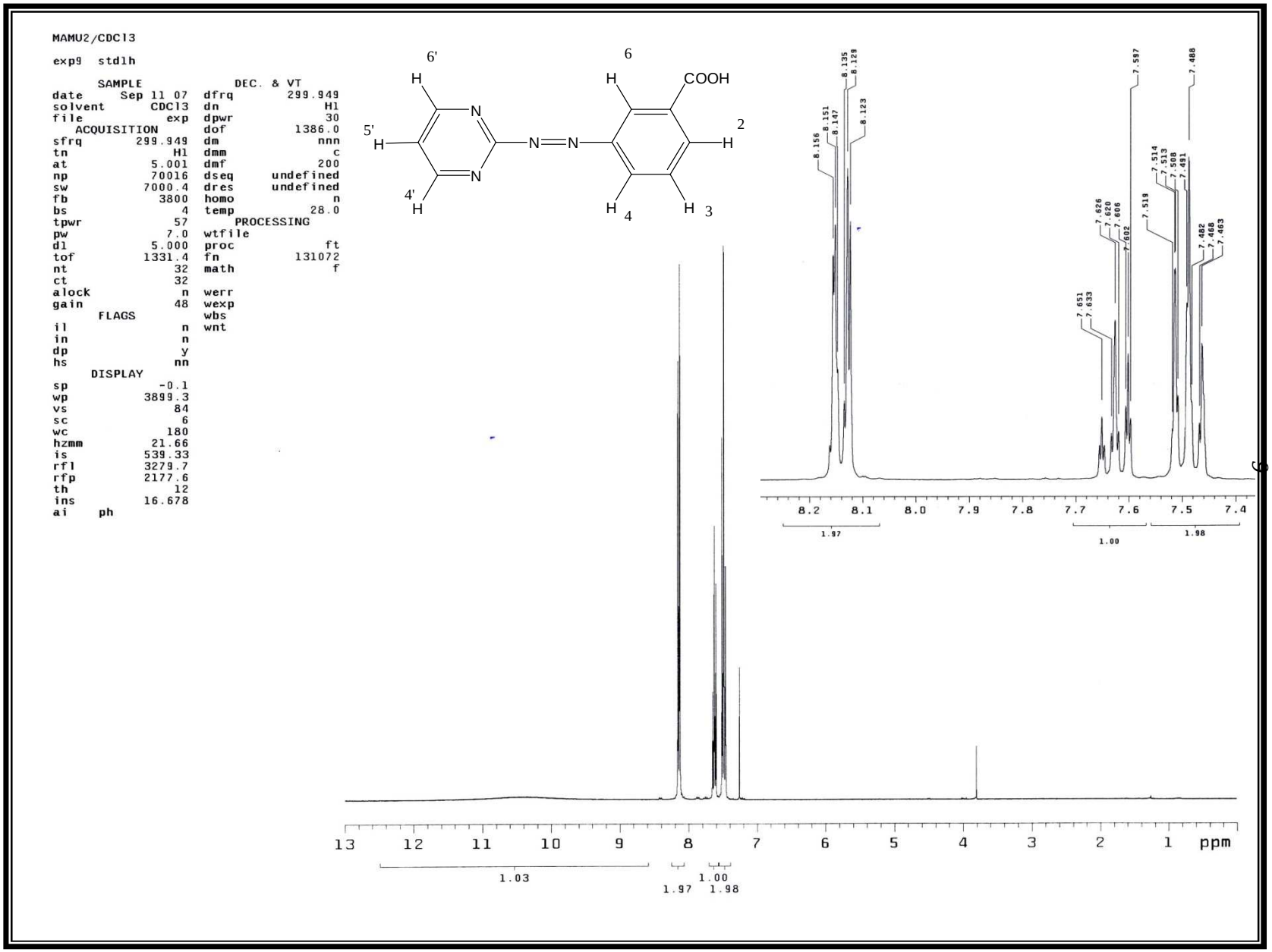


Figure 1: ^{1}H-NMR spectrum of compound 1

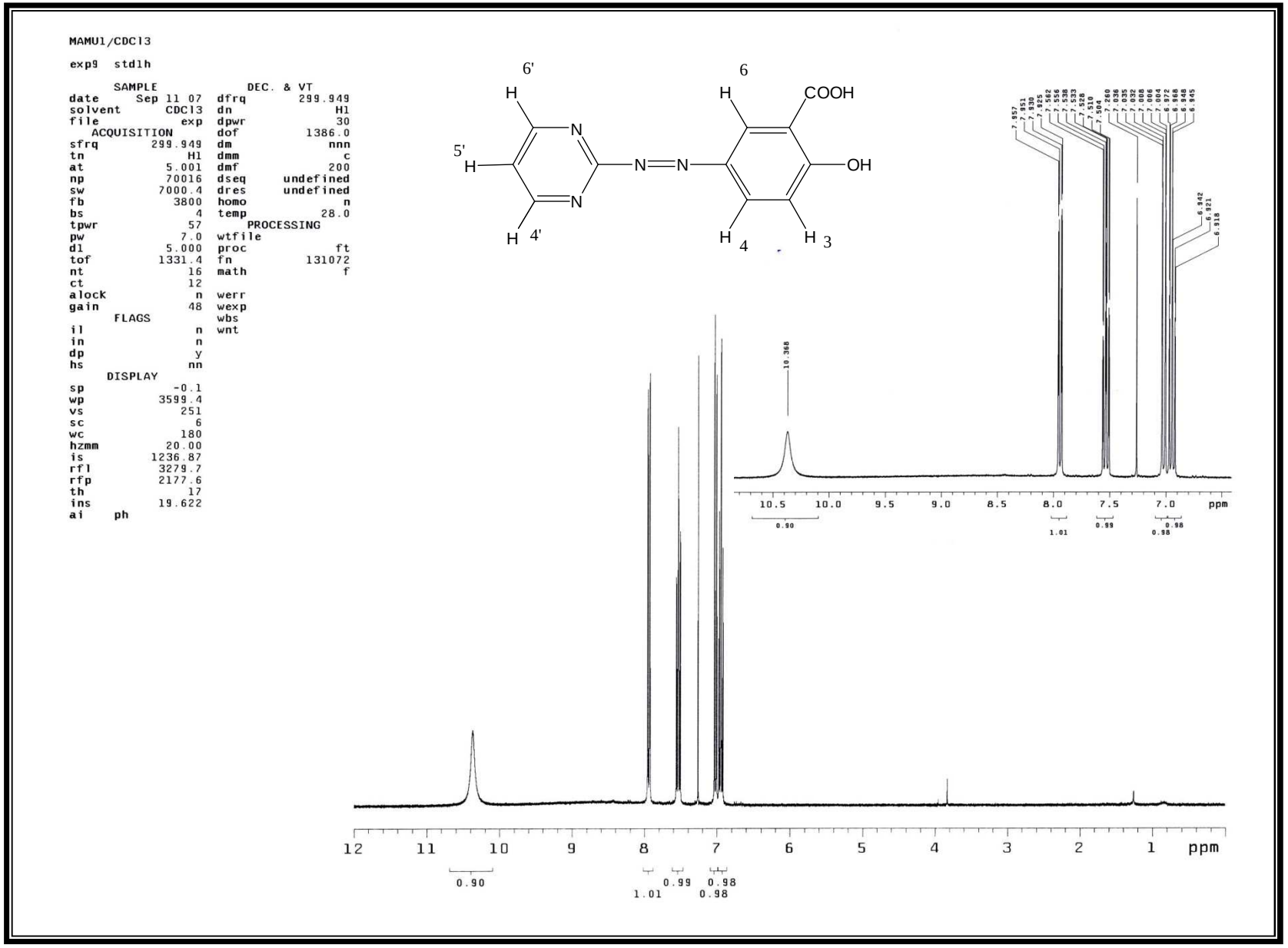


Figure 2: ^{1}H-NMR spectrum of compound 2

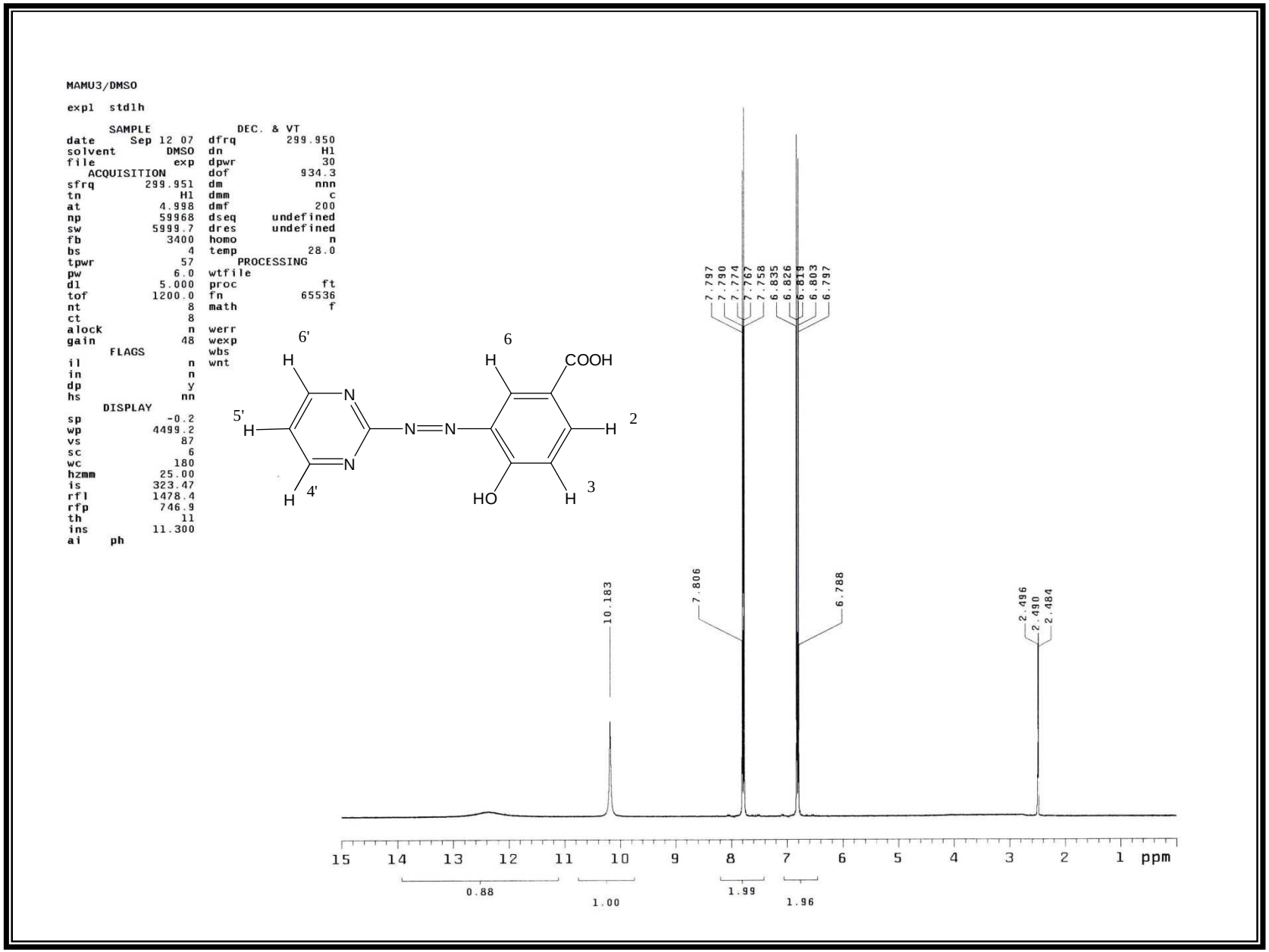


Figure 3: ^{1}H-NMR spectrum of compound 3

4. Conclusion

Some of new azo compounds were prepared and identified by IR spectroscopy which showed stretching vibration of azo group in the range 1540-1565 cm^{-1}. ^{1}H-NMR spectra showed the protons of pyrimidine ring in the downfield than phenyl protons and characteristic singlet signals for OH and COOH protons.

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الملخص

تم تحضير اربعة من مركبات آزو الجديدة المشتقة من امينو بايريمدين و كل من حامض البنزويك وحامض الساليسليك و بارا–هيدروكسي حامض البنزويك و ريسورسينول. وشخصت المركبات المحضرة باستخدام مطيافية الاشعة تحت الحمراء ومطيافية الرنين النووي المغناطيسي البروتوني.