

New Nitro Diazo Dye Vanillin Derivatives, Synthesis and Characterization

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Abstract

The diverse applications of azo compounds as reagents to bring about chemical synthesis is one of the fastest-growing areas of research. It is well known that the position of the substituents has an important role in the effect of the medicinal, dye industry, thermal, and optical properties of the compounds. In this work, we limit our studies to synthesizing two new diazo dye vanillin derivatives starting from aniline. Nitro aniline compounds **10** and **12** were prepared starting from aniline, and new nitro diazo vanillin derivatives were obtained **4** and **5**. Through coupling reactions with vanillin **15** *via* diazonium salts, 4-hydroxy-3-methoxy-5-((2,4-dinitrophenyl)diazenyl)benzaldehyde **4** was obtained from 2,4-dinitroaniline **10**, while 4-hydroxy-3-methoxy-5-((2,4,6-trinitrophenyl)diazenyl)benzaldehyde **5** resulted from 2,4,6-trinitroaniline **12**. The synthesized compounds were characterized by spectroscopic methods; UV-Vis., FTIR, MS, and ¹HNMR and melting point determination. The results of the reactions gave good yields of all products.

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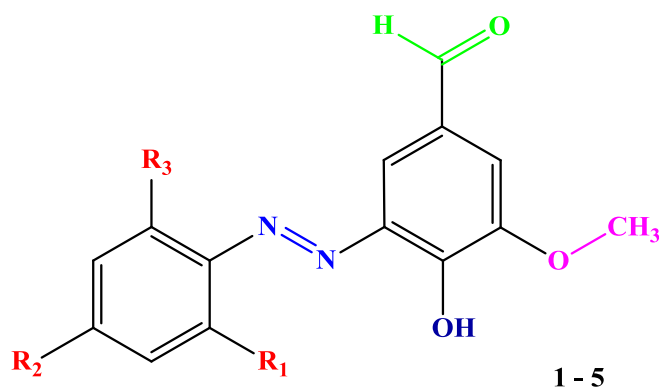


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1. Introduction

The nitro-functional group is one of the common groups in the organic syntheses. It is simple to synthesize in the aromatic rings. It is commonly used organic compounds that have nitro functional groups in synthetic dyes, which are found in foods, plastics, pharmaceuticals, drugs, and many other fields. Some compounds raised biological activities in the presence of the nitro functional groups [1-3] or vanillin main core [4]. Recently, we have synthesized three compounds **1-3** with the nitro functional groups in diazo dye vanillin derivatives and their biological activities against some microbes were studied [5], Figure 1. Each of the dipole-dipole interactions bending [6], the molecular and the spectroscopic structures by using the computational DFT method [7], the biophysical properties of the interactions with Human Serum Albumin [8], and the molecular docking as antiviral candidates of COVID-19 [9] were studied. Continuously our investigation for nitro diazo dyes, we were synthesized in the present work, another two new nitro diazo dye vanillin derivatives **4** and **5**, Figure

1, and characterized by using m.ps., UV-Vis., FTIR, MS, and NMR spectroscopic methods.



- 1: R₁ = NO₂, R₂ = H, R₃ = H.
- 2: R₁ = H, R₂ = NO₂, R₃ = H.
- 3: R₁ = NO₂, R₂ = H, R₃ = NO₂.
- 4: R₁ = NO₂, R₂ = NO₂, R₃ = H.
- 5: R₁ = NO₂, R₂ = NO₂, R₃ = NO₂.

Figure 1. The chemical structures of the nitro diazo dye vanillin derivatives **1-5**.

2. Experimental Part

2.1. General

The melting points were determined on the Electrothermal Apparatus. The UV-Vis. spectra were recorded with A-580, double beam Spectrophotometer. FTIR spectra ($4000\text{--}400\text{ cm}^{-1}$) were performed as KBr pellets on a Nicolet IS10 FTIR Spectrometer. Mass spectra were carried out on the Direct Inlet part to the mass analyzer in Thermo Scientific GC/MS model ISQ, and ^1H NMR spectra were recorded on JEOL's spectrometer operating at 500 MHz, using $\text{DMSO-}d_6$ as a solvent and TMS as internal standard [10].

2.2. Synthesis

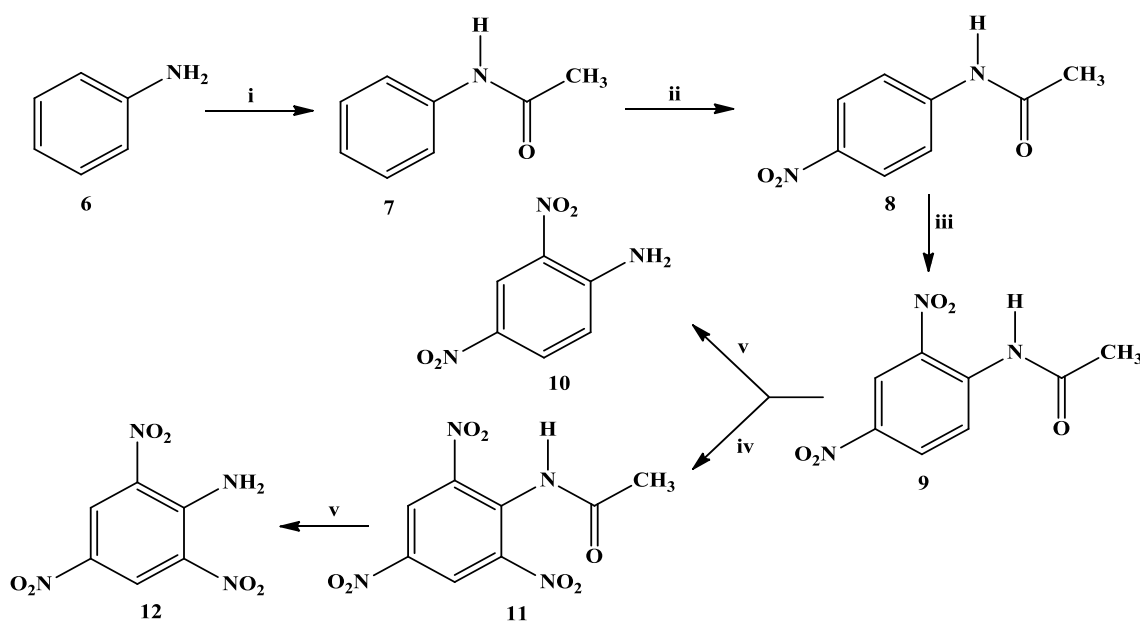
Both nitro diazo dye vanillins **4-5** were synthesized in multistep. The acetanilide **7** was first obtained from aniline **6**, after that it was undergone to the nitration reaction in which compound **8** was resulted, then by double nitration to 2,4-dinitro acetanilide **9**. In the third step, 2,4-dinitro acetanilide reduction to 2,4-dinitroaniline **10** as described previously [5].

3. Results and Discussion

All synthesized compounds **7-12** are characterized by comparing their spectroscopic data and melting points with the literature survey. Some physical properties of **4** and **5** are summarized in Table 1. Azo-coupling reaction of 2,4-dinitroaniline **10** and 2,4,6-trinitroaniline **12** with vanillin **15** give new compounds **4** and **5**, respectively, Schemes 1 and 2.

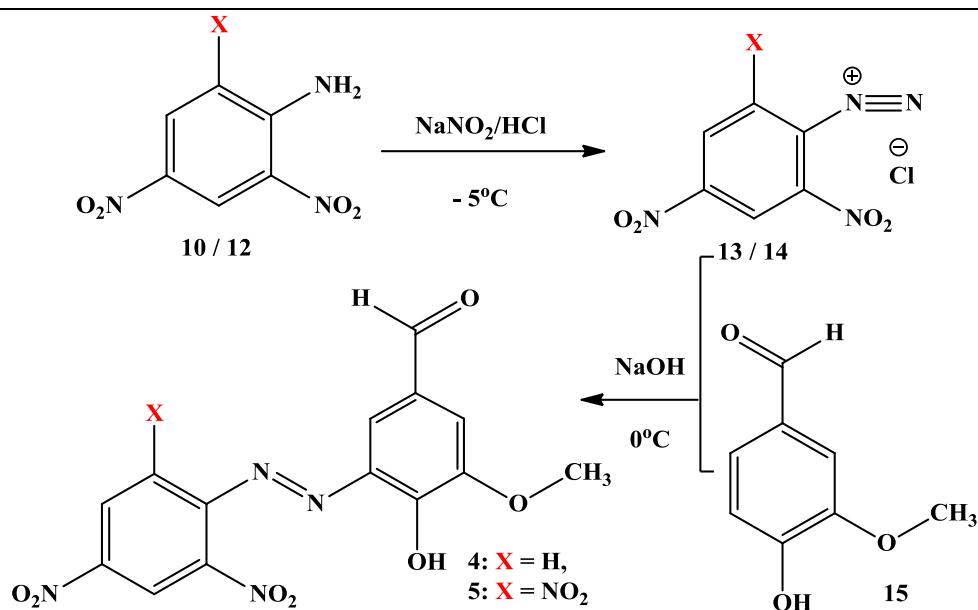
Table 1: Physical Properties of compounds **4** and **5**:

#	M.F.	M.W. g/mol	m.p. °C	Physical State	Yield %
4	$\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_7$	346.26	116.3	Light brown	49.1
5	$\text{C}_{14}\text{H}_9\text{N}_5\text{O}_9$	391.26	141.0	Red	57.5
7	$\text{C}_8\text{H}_9\text{NO}$	135.16	114	White crystals	77.8
9	$\text{C}_8\text{H}_7\text{N}_3\text{O}_5$	225.16	140	Orange brown	60.9
10	$\text{C}_6\text{H}_7\text{N}_3\text{O}_4$	183.12	116	Brown	85.3
11	$\text{C}_8\text{H}_6\text{N}_4\text{O}_7$	270.16	120	Redish orange	43.3
12	$\text{C}_6\text{H}_4\text{N}_4\text{O}_6$	228.12	104	Red	76.2



- i. $\text{Ac}_2\text{O}/\text{H}_2\text{O}$, $\text{CH}_3\text{CO}_2\text{Na}\cdot 3\text{H}_2\text{O}$, HCl, 20 min., rt.
- ii. AcOH , H_2SO_4 , HNO_3 , 20 min., 5°C then 30 min., rt.
- iii. H_2SO_4 , HNO_3 , 15 min., $15\text{--}20^\circ\text{C}$ then 3 days darkness, rt.
- iv. H_2SO_4 , HNO_3 , 10 min., $25\text{--}30^\circ\text{C}$ then 5 days darkness, rt.
- v. $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$, reflux, 30 min., then neutralize by 9 M NaOH, pH 4-5.

Scheme 1. The general route to prepare **10** and **12**.



Scheme 2. The general route to prepare 4 and 5.

The FTIR spectrum of compound 4 showed a stretching vibration band around 3332 cm^{-1} due to the hydroxyl functional group. It also contained a stretching vibration band at 1680 cm^{-1} proving conjugated C=O. Both peaks at 2765 and 2830 cm^{-1} indicated the absorption of the aldehydic hydrogen. Including, the C=C stretching of benzene rings appeared at 1631 cm^{-1} , and the C-H stretching at 3087 cm^{-1} indicated a saturated methyl group, Figure 2a. The mass spectrum of 4, Figure 3 which showed a fragment $m/z = 346.33$ was assigned to the molecular ion and confirmed the molecular formula of $\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_7$. Another fragment at $m/z = 330.93$ and 195.36 resulted by losing methyl group and $\text{C}_8\text{H}_7\text{O}_3$ radicals, respectively.

Compound 5 was formed in four perpetrated steps. In the first 2,4-dinitroacetanilide 9 converted to 2,4,6-trinitroacetanilide 11 by nitration reaction. Then through the reduction reaction of compound 11 the 2,4,6-trinitroaniline 12 was obtained. A new compound 5 produced through the azo-coupling reaction of 2,4,6-trinitroaniline 12 with vanillin. The preparations compound 11 and 12 are characterized by comparing their spectroscopic data and melting points with the literature. The FTIR spectrum of compound 5 is depicted in Figure 2b. The spectrum exhibited an absorption at 3319 cm^{-1} indicating the O-H stretching vibration. The strong absorption at

1633 cm^{-1} is attributed to a carbonyl functional group. A weak band around 2740 cm^{-1} may be for C-H aldehydic proton.

The C=C in benzene rings were given stretching vibrations at 1589 cm^{-1} , while the C-H frequencies of the same rings were observed at 3084 cm^{-1} . The spectrum also showed strong peaks at 1529 cm^{-1} and 1348 cm^{-1} , which correspond to asymmetrical and symmetrical stretching absorption of nitro group. Other important peaks were observed at 1589 cm^{-1} and 1421 cm^{-1} due to $\nu_s\text{-N=N-}$ modes of symmetric and asymmetric azo functional groups [11,12]. The important peaks in the $^1\text{HNMR}$ spectrum of 4 are shown in Figure 4a. The singlet at $\delta 3.2$ ppm was attributed to the three protons of the methyl functional group. The singlets of the three aromatic protons of the nitrobenzene ring were observed at $\delta 8.784$ ppm and 7.927 ppm. The peaks at around $\delta 7.937$ and 7.399 ppm were assigned to the two protons in the benzaldehyde ring. The singlet of the aldehydic proton appeared at $\delta 10.5$ ppm.

The $^1\text{HNMR}$ spectrum of compound 5 Figure 4b showed two singlet peaks at $\delta 2.65$ and 3.6 ppm belonging to methyl and hydroxyl functional groups, respectively. The signals between were assigned to the four protons of the aromatic rings. The peak for the aldehydic proton exhibited at $\delta 9.99$ ppm.

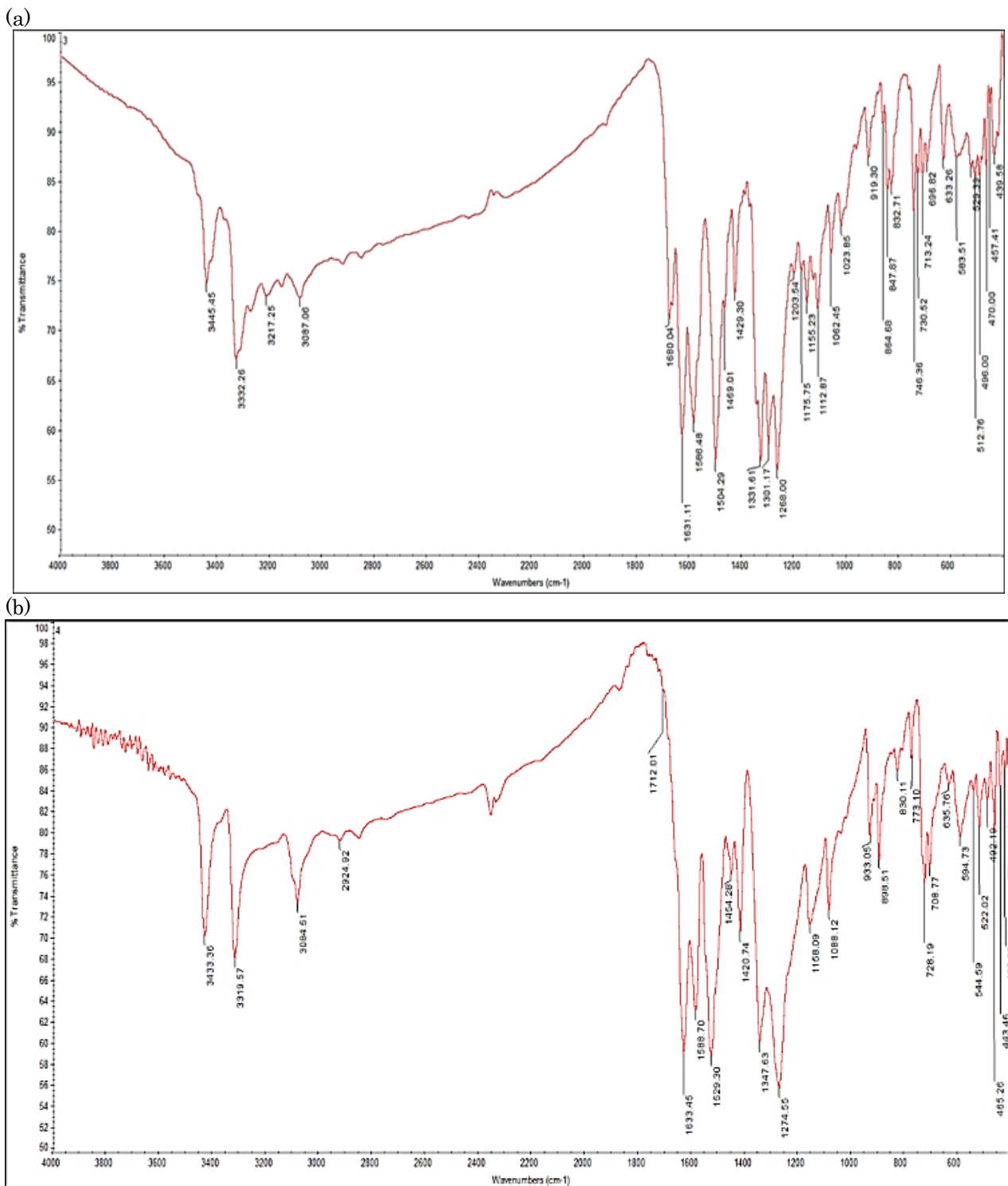


Figure 2. The FTIR spectra of: a. 4; and b. 5.

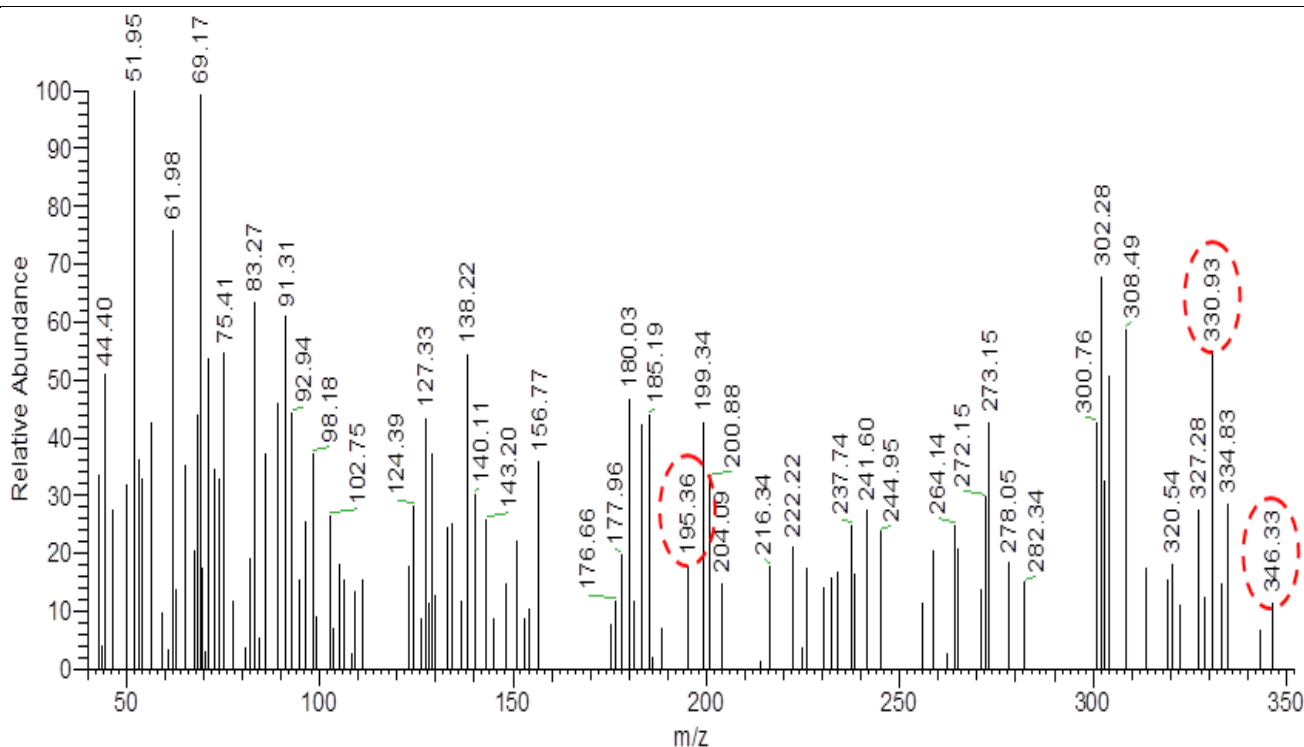


Figure 3. The mass spectra of 4.

The main difference between the ^1H NMR spectra of compounds 4 and 5 is only the integration of protons in the benzene ring that contained nitro groups. In compound 4 there were three protons, while compound 5 spectrum showed two protons.

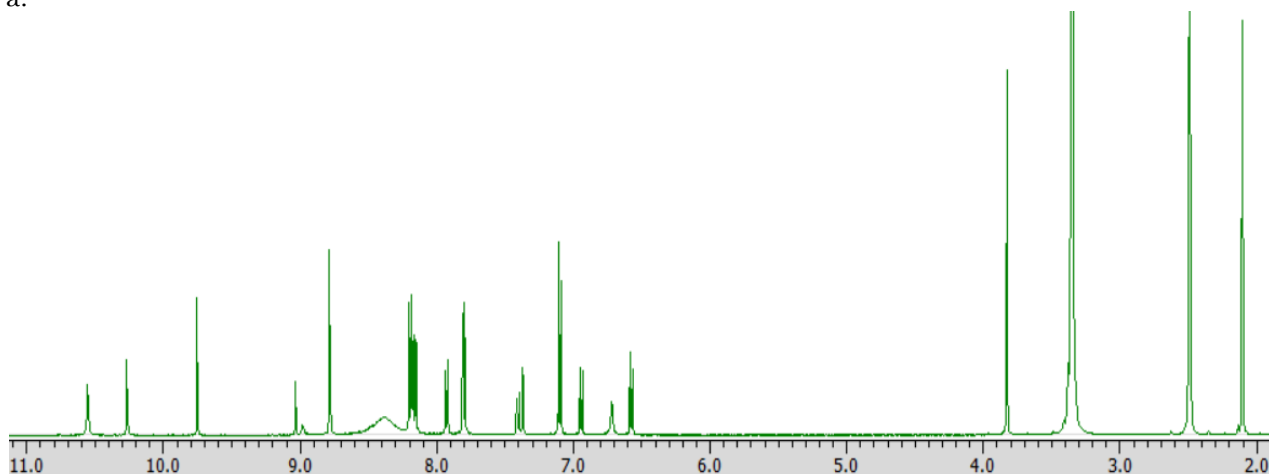
On the other hand, the mass spectrum confirmed the suggested structure of compound 5. The suggested structure was confirmed by MS spectrum Figure 5 which contained fragments at m/z 240 and 151 corresponding to $\text{C}_6\text{H}_2\text{N}_5\text{O}_6$ and $\text{C}_8\text{H}_7\text{O}_3$, respectively.

The UV-Vis spectra of 4 and 5 were studied in ethanol, Figure 6. Two bands appeared in the spectrum of 4, the first band around 205 nm due to $\pi \rightarrow \pi^*$ electronic transition of the benzene ring, whereas the second band was between 285 and 445 nm resulting from $\pi \rightarrow \pi^*$ electronic transitions of

azo functional group $-\text{N}=\text{N}-$. Also, the spectrum at 330 nm showed maximum absorption for the azo functional group.

While the UV-Vis spectrum of 5 exhibited bands $\pi \rightarrow \pi^*$ at 210 nm due to the benzene ring. The second band between 285-365 nm with maximum absorption might result from $\pi \rightarrow \pi^*$ electronic transition due to trinitro benzene and vanillin aromatic rings, while the third band around 365-450 nm is possible due to intramolecular charge-transfer and azo functional group $-\text{N}=\text{N}-$ where results from $\pi \rightarrow \pi^*$ electronic transitions between trinitro phenyl and vanillin through the $-\text{N}=\text{N}-$ as a bridge, and the maximum absorption showed at 400 nm. All these data support the structures of both compounds 4 and 5.

a.



b.

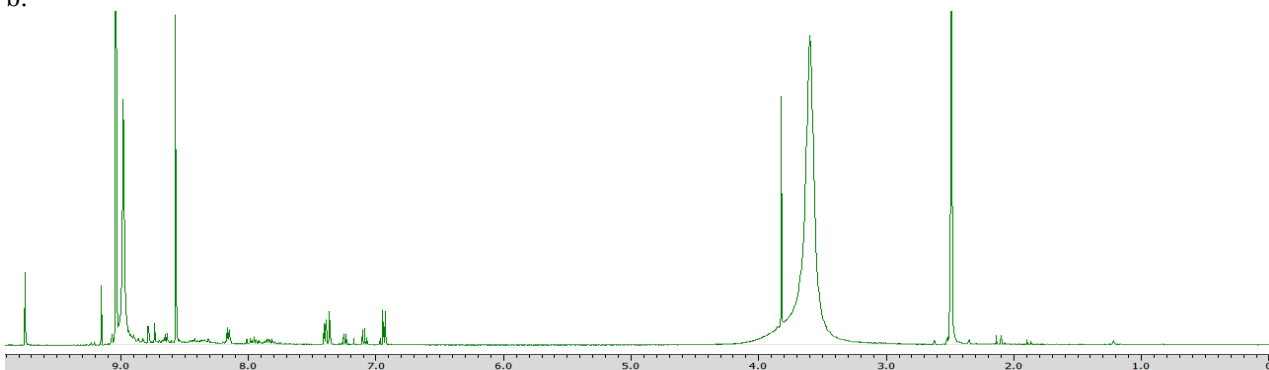


Figure 4. The ^1H NMR spectroscopy of a. 4 and b. 5.

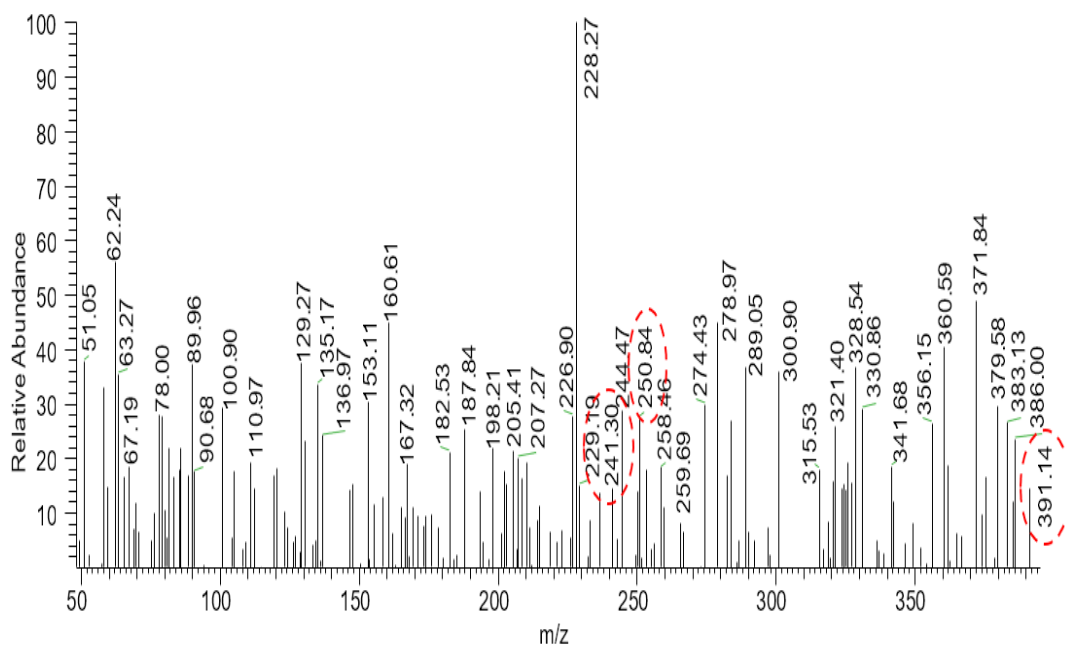


Figure 5. The mass spectra of 5.

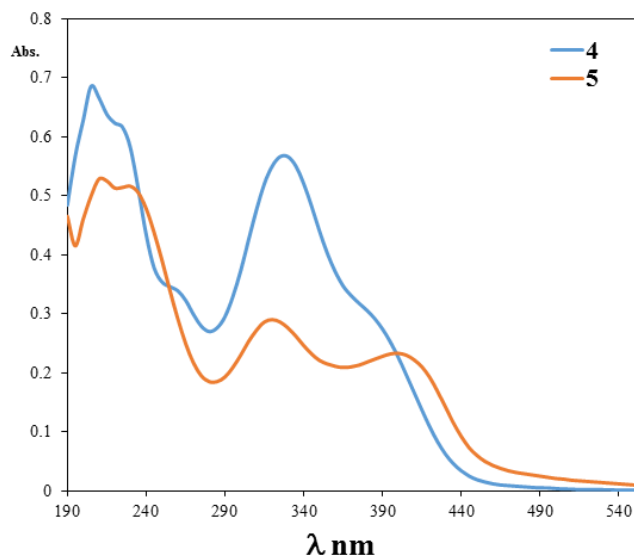


Figure 6. The UV-Vis spectra of 4 and 5.

4. Conclusions

We have synthesized two new nitro dye compounds containing azo groups *via* coupling reactions between diazo nitro compounds and vanillin. The diazo nitro compounds were obtained through some preparations that started from aniline which was acylated to acetanilide, then *via* separation processes the acetanilide converted to 2,4-dinitro acetanilide and 2,4,6-trinitro acetanilide, finally by reduction reactions the 2,4-dinitroaniline and 2,4,6-trinitroaniline were formed. Both nitro anilines converted to diazo compounds and used in the condensation reaction with vanillin to produce the new azo dye vanillin Derivatives. The spectroscopic analysis studies include FTIR, ¹HNMR, MS, and UV-Vis techniques suggest that the new compounds are 4-hydroxy-3-methoxy-5-((2,4-dinitrophenyl) diazenyl)benzaldehyde 4 with yield percentage 49%, and 4-hydroxy-3-methoxy-5-((2,4,6-trinitro phenyl) diazenyl) benzaldehyde 5 with yield percentage 57%.

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