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Formation, Characterization and Microscopic Study of Four- and Five-membered Ring

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Abstract

Types of organic compounds are famous for many industrial and medical applications, including azo compounds, one of the largest groups involved in the manufacture of various organic compounds. For example, they are considered as initiators of free radicals in the polymerization reactions of alkenes used in the manufacture of plastics. Most of cyclic compounds have nano properties which make this type of compound important in organic field. It is also used in dyeing woolen and cotton fabrics, synthetic fibers, and leather. Its effectiveness has been proven because its complexes are high-quality dyes. It is also considered important in analytical chemistry for the determination of ions in their solutions and in extraction processes. Azo compounds and their derivatives have proven their great importance from a biological standpoint, as antibacterial, antifungal, and many types of cancer cells, in addition to their importance as antioxidants. A number of practical techniques have been used to carousal their chemical structures which delivered to strong indications of their chemical structures through different technical plans and chemical spectra like (FT IR-Spectra, 1H.NMR-Spectra, 13C.NMR-Spectra), melting points, other studies represented by microscopic studies, nitrogen cyclic compounds are considered industrial compounds in the fields of corrosion, as well as in the manufacture of paint and the manufacture of some types of coatings used against rust. Therefore, their importance has increased in the recent period. These compounds are also characterized as effective materials for preparing dyes for woolen fabrics and wall dyes, so they are industrial materials and pharmaceutical materials as well.

Keywords: Four ring, microscope, azo, imine, structure

INTRODUCTION

Dyes are usually given two terms (pigments and dyes), thus, (pigments) are those dyes that retain their crystalline or molecular structure during the process of their use and have a special crystalline form [1]. As for (dyes), they are used to refer to dyes that lose their structural characteristics during the process of their use. Through the process of decomposition or evaporation, the term “dyes” is often used for dyes used in textile industries and for coloring foodstuffs [2, 3], while the term “pigments” is used for dyes used in paint materials, cosmetics, and in the ink industry. Azo compounds have strong, clear colors such as yellow, red, and orange [4–6]. They are used as dyes, and the most common are diazo dyes. Azo compounds are considered among the most widely used dyes, constituting more than 60% of all types of dyes. They are colored materials that can adhere to the materials to be dyed in multiple ways to give them bright colors that are resistant to acids, bases [5–7], washing, light, and air. They are highly stable and quick to react with metal ions, in addition to their high sensitivity and selectivity, these dyes are characterized by many features, including the color quality, as they have bright

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colors of high intensity and their colors range from yellow to blue [8–12], which depend on the successive π system in the molecule. They also have high molecular weights and high melting points, which led to their use in wide areas of chemistry [13]. Azo compounds are considered one of the largest groups involved in the manufacture of various organic [14–16] compounds. For example, they are considered as initiators of free radicals in the polymerization reactions of alkenes used in the manufacture of plastics. As for the aromaticity of these compounds, they are used as acid-base indicators, such as methyl red, methyl orange, and Congo red. It is also used in dyeing woolen and cotton fabrics [17–19], synthetic fibers, and leather. Its effectiveness has been proven because its complexes are high-quality dyes [20, 21]. It is also considered important in analytical chemistry for the determination of ions in their solutions and in extraction processes [22].

Instruments and Experimental Part

The infra-red spectra were recorded in the frequency range (4000–400) cm-1 using KBr disc by using (8400 SFTIR SHIMADZU spectrophotometer). The spectra of 1 HNMR and 13CNMR were recorded BRUKER AV 400 Avance-III (400 MHz and 100 MHz), Iran, using DMSO-d6 as the solvent, and microscopic studies.

Methods and Instruments

Formation of Azo Compound {1}

The azo compound was prepared using the method known by several researchers in the field of preparing reagents, including the method of precipitation of the diazo salt after adding the acid to the primary amine, and after the process of forming the azo salt [23, 24], the process of coupling between it and the reactant was completed to form a new compound {1} by following procedures in literatures [13,14] as depicted in Figure 1.

Formation of Azo-Schiff Base Derivative {2}

Azo compound {1} (0.01 mol) refluxed with (0.04 mol) of p-nitro amine for (4 h) with (a few drops) of glacial acetic acid and absolute ethanol (50 ml), the product filtered, dried [25, 26], recrystallized to yield Azo-Imine Derivative {2} according to procedures [13,14] shown in Figure 2.

Preparation of Azo-Cyclic Derivative {3}

Azo-Imine compound {2} (0.01 mol) refluxed with (0.04 mol) of chloro acetyl chloride for (7 h) with triethyl amine with chloroform, then rotation for (3 h), the product filtered [27, 28], dried [27, 28], recrystallized to yield Azo-four membered derivative {3} according to procedures [13,14].

Preparation of Azo-Cyclic Derivative {4}

Azo-Imine compound {2} (0.01 mol) refluxed with (0.04 mol) of mercapto acetic acid for (6 h) with ethanol (40 ml), the product filtered, dried [29, 30], recrystallized to yield Azo-five membered derivative {4} according to procedures [13, 14].

Preparation of Azo-Cyclic Derivative {5}

Azo-Imine compound {2} (0.01 mol) refluxed with (0.04 mol) of mercapto acetic acid for (6 h) with ethanol (40 ml), the product filtered, dried [31, 32], recrystallized to yield Azo-five membered derivative {5} according to procedures [13, 14].

Formation of compound {3}, {4}, and {5} is shown in Figure 3.

RESULTS AND DISCUSSION

Several studies were carried out to improve these compounds by the using of spectral identification like: 1H.NMR spectra, FT.IR-Spectra, C.NMR-Spectra, other studies represented by (Melting points), other studies represented by physical with chemical properties, and microscopic studies [33–37], all the results are shown in Tables and Figures.

Chemical Identification

FT.IR-Spectra: The first characterization of derivatives is appearance band of azo group at (1498, 1588) for (-N=N-) and carbonyl of ketone (-CO-) at (1710) in compound {1}, but in compound {2} appeared band of (CH=N-) Imine group at (1620) Cm^{-1} and azo group at (1498, 1589) in compound {2} and bands for nitro group [38, 39] appeared at (1398, 1500) Cm^{-1}, all frequencies clarified according to Aseel MJ, et al. [30] as identification reference of all spectra, and other functional groups in Figures (4–8):

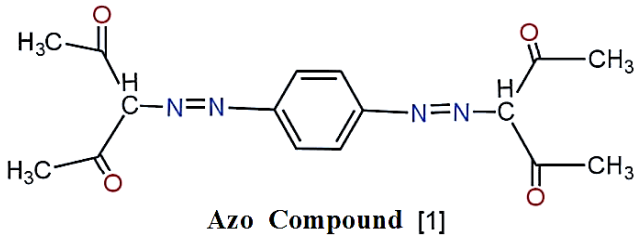

Figure 1. Formation of Azo-compound {1}.

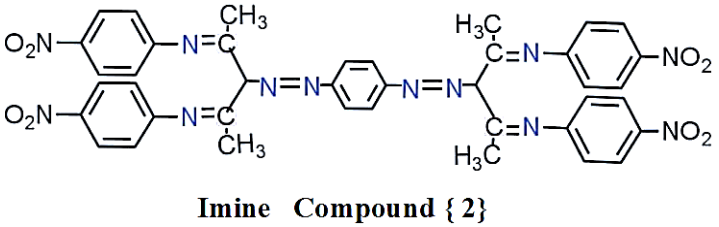

Figure 2. Formation of Schiff base compound {2}.

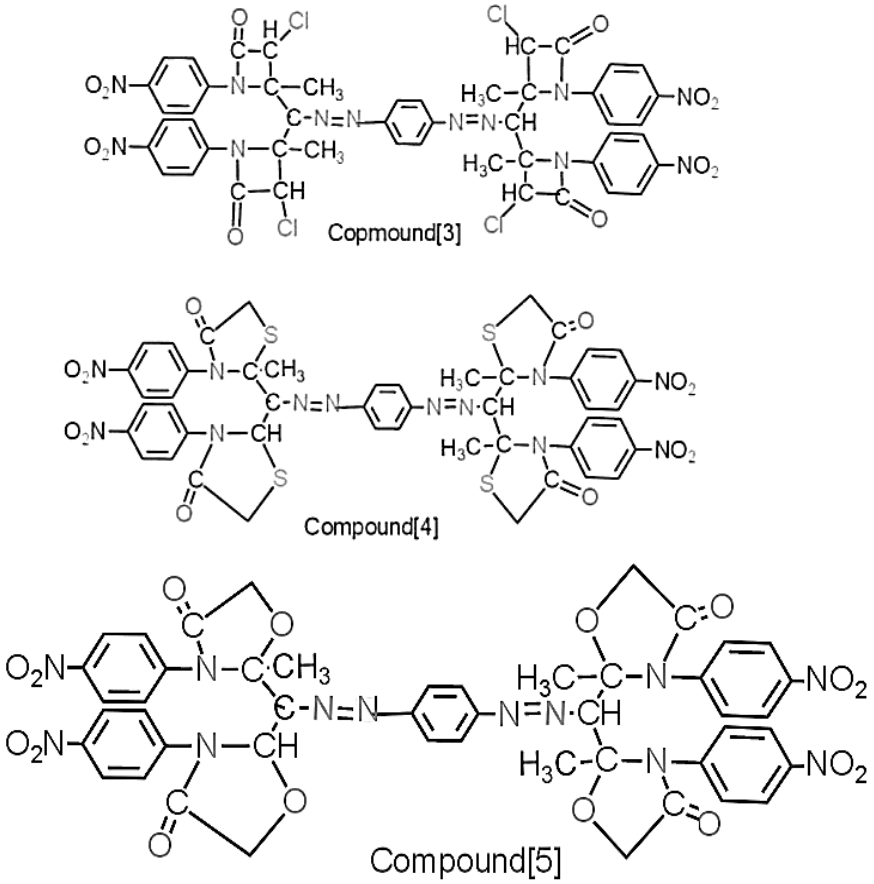

Figure 3. Formation of Azo-compounds {3, 4, 5}.

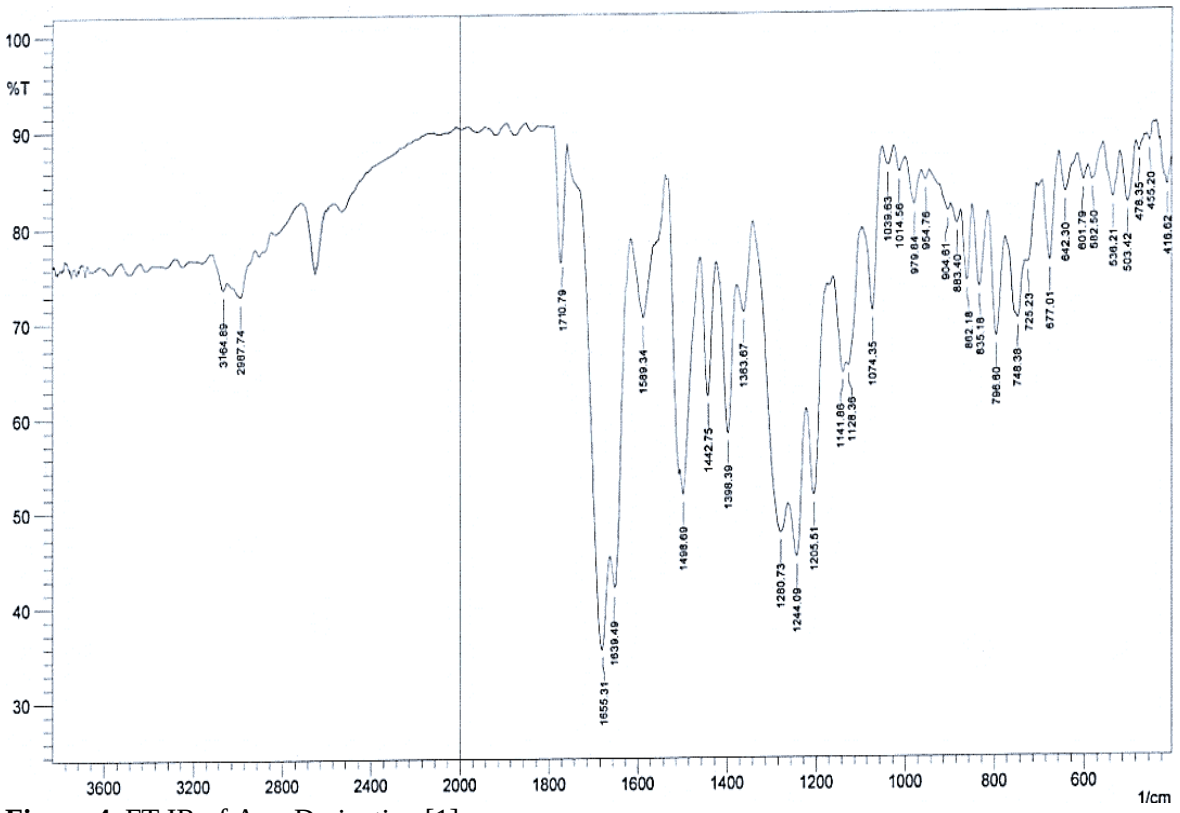

Figure 4. FT.IR of Azo-Derivative [1].

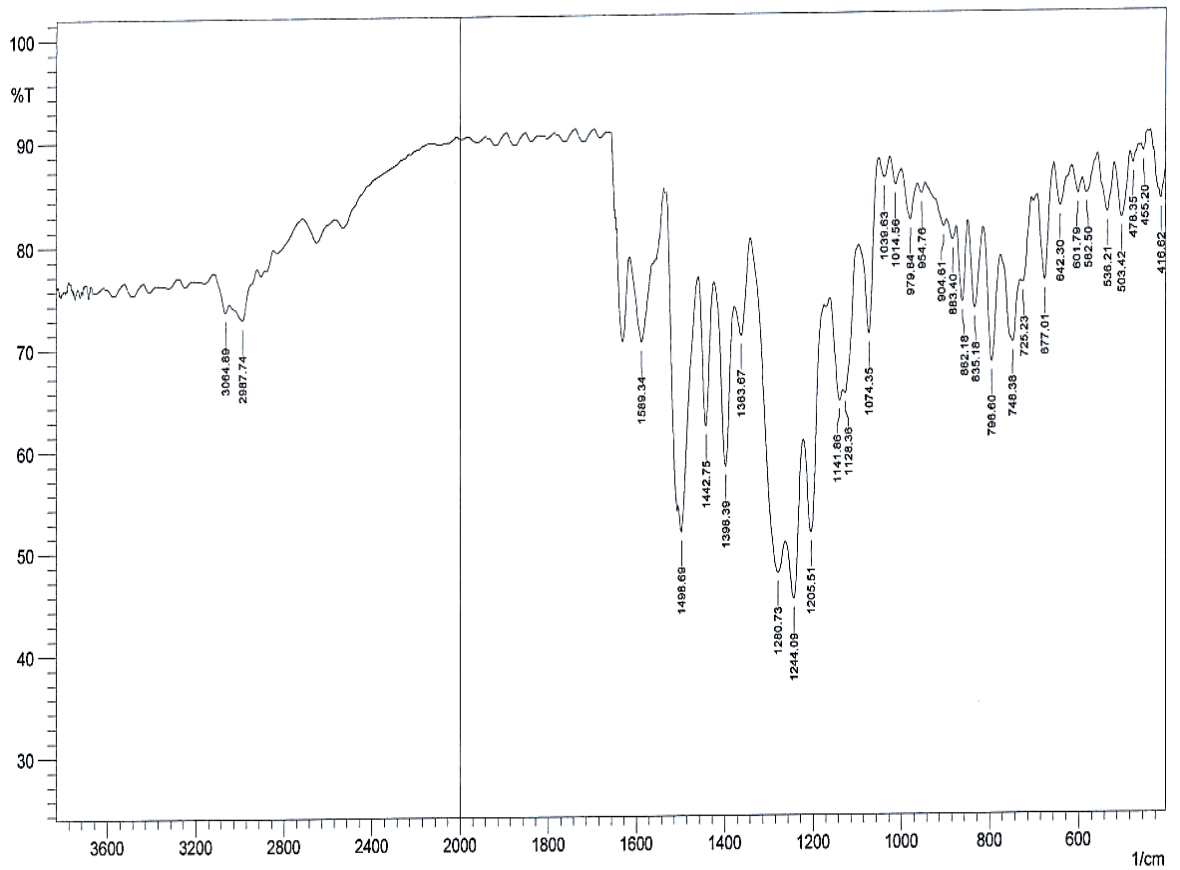

Figure 5. FT.IR of Azo-Imine derivative [2].

1H.NMR-Spectra: By following the signals of the resonance spectra, we noticed the emergence of signals belonging to the protonation of the aldamine group, which are clear and sharp signals indicating that the reaction took place [40–42]. As for the compounds formed, these signals disappeared as a result of the reaction to form new peaks in the resulting compounds, all peaks enlightened bestowing to reference as identification reference [30] of all spectra results of HNMR of all compounds have shown in Figures 9–13.

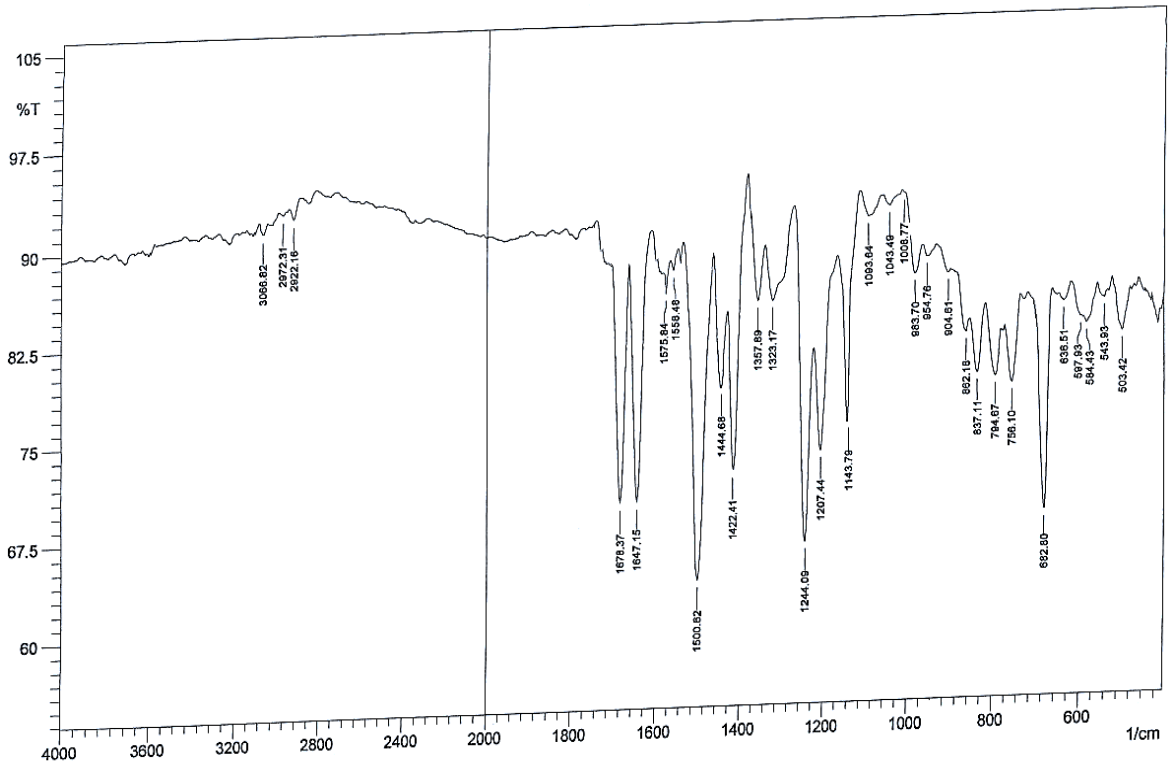

Figure 6. FT.IR of Azo-Cycle derivative [3].

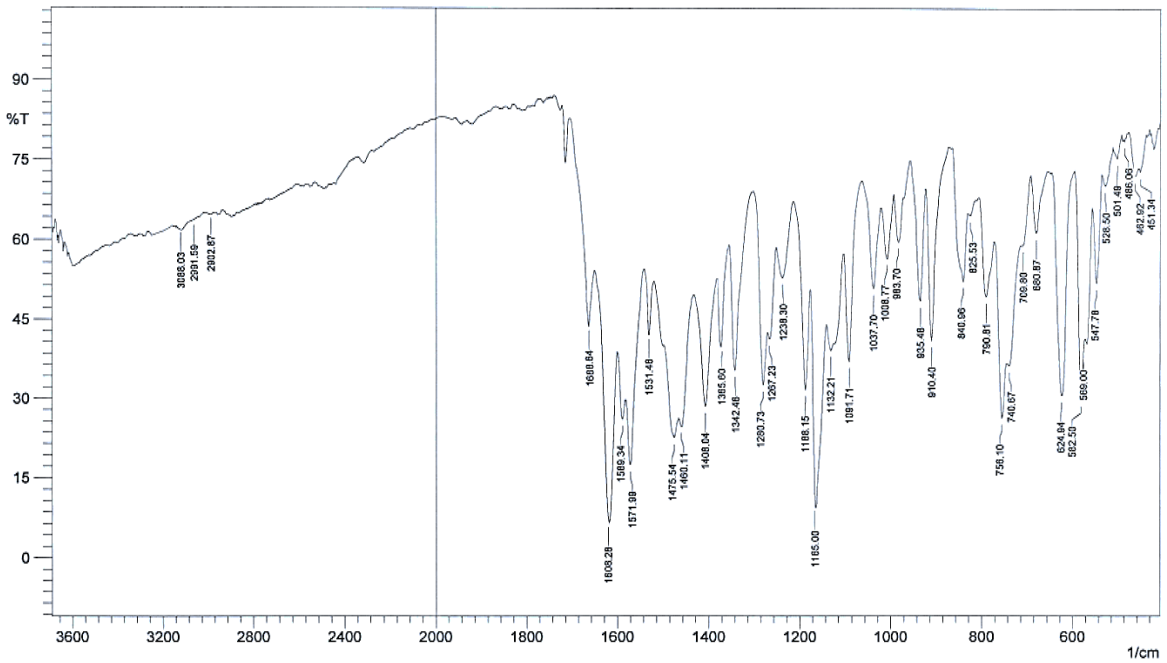

Figure 7. FT.IR of Azo-cycle derivative [4].

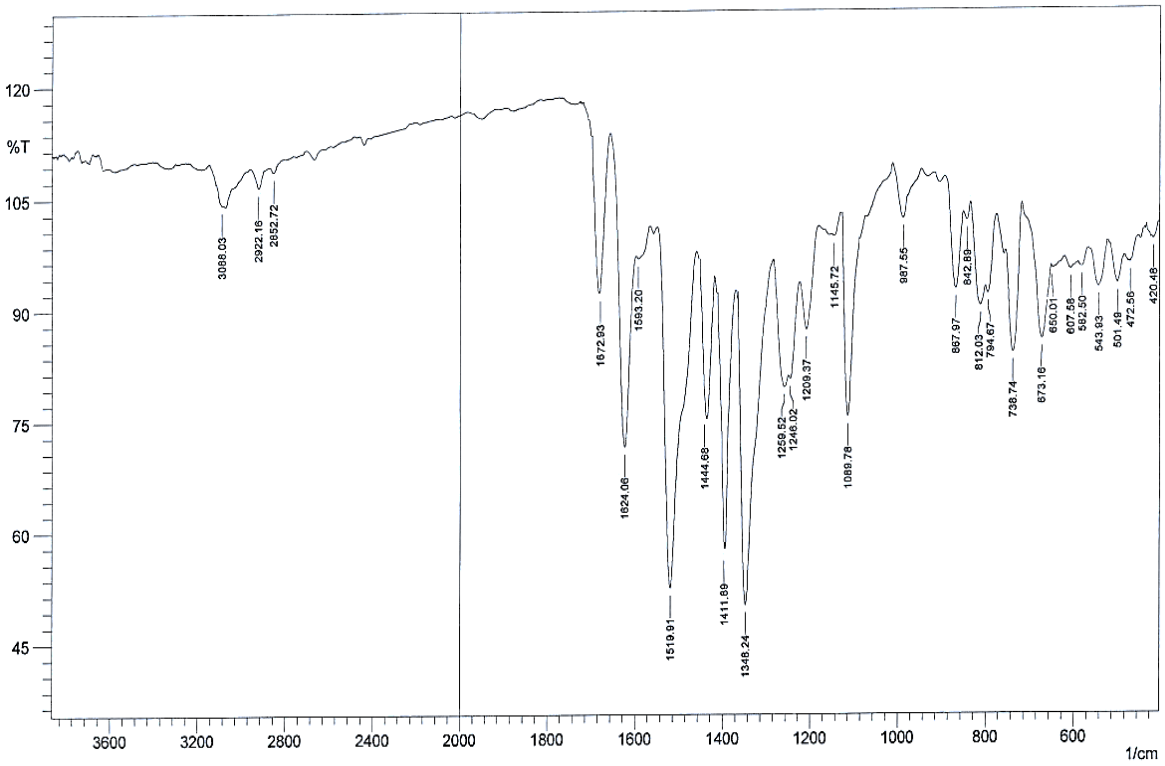

Figure 8. FT.IR of Azo-cycle derivative [5].

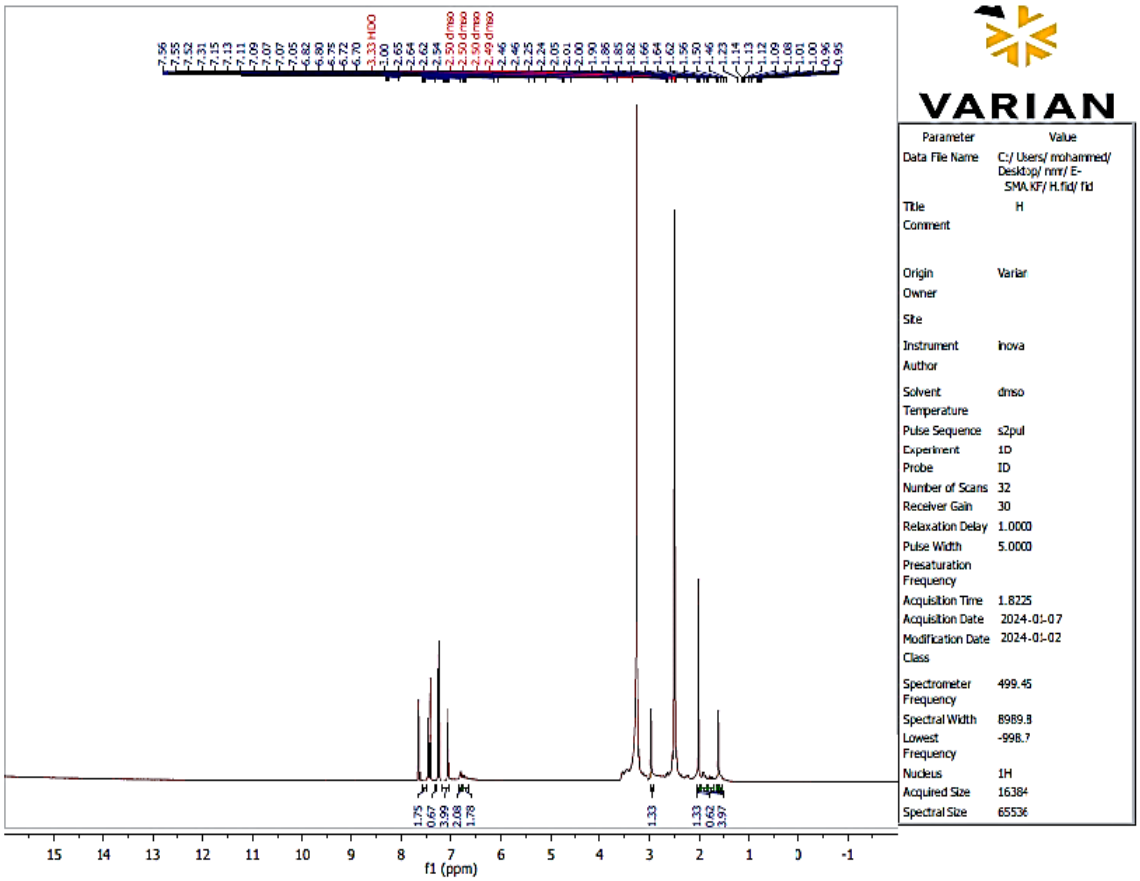

Figure 9. H.NMR-Spectrum of Azo-Derivative [1].

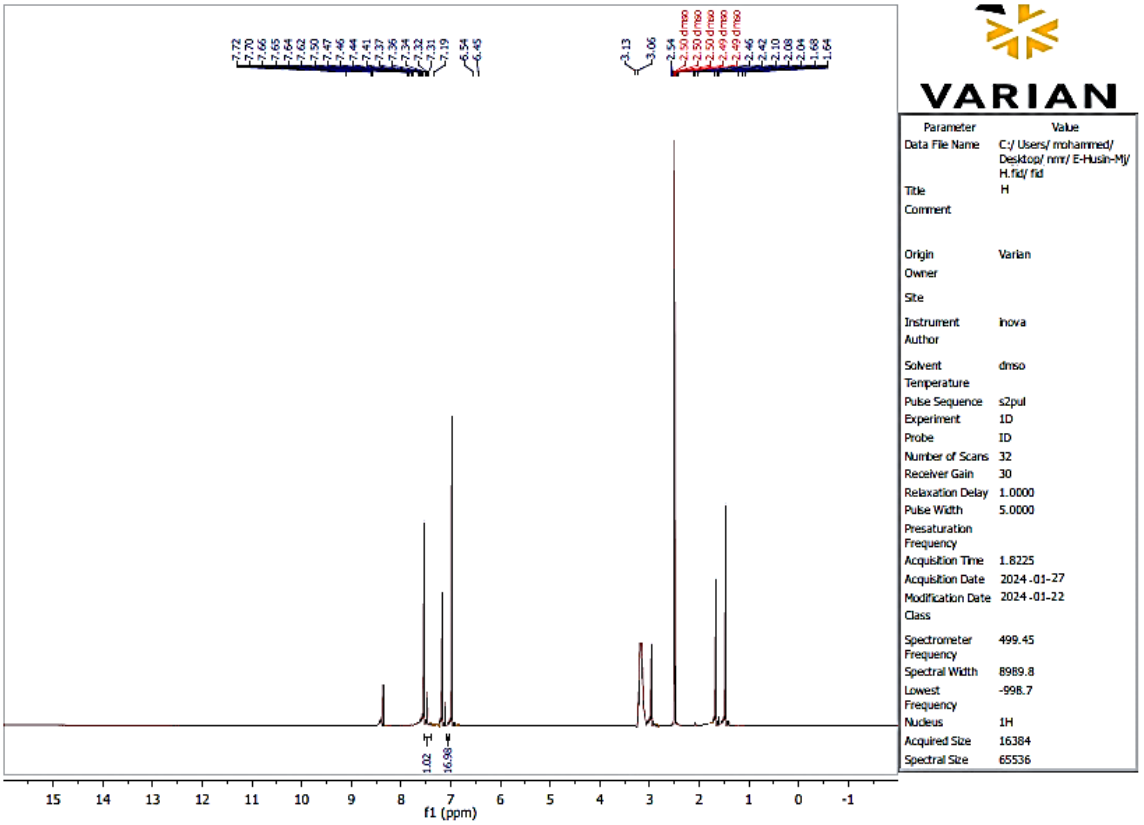

Figure 10. H.NMR-Spectrum of Azo-Imine derivative [2].

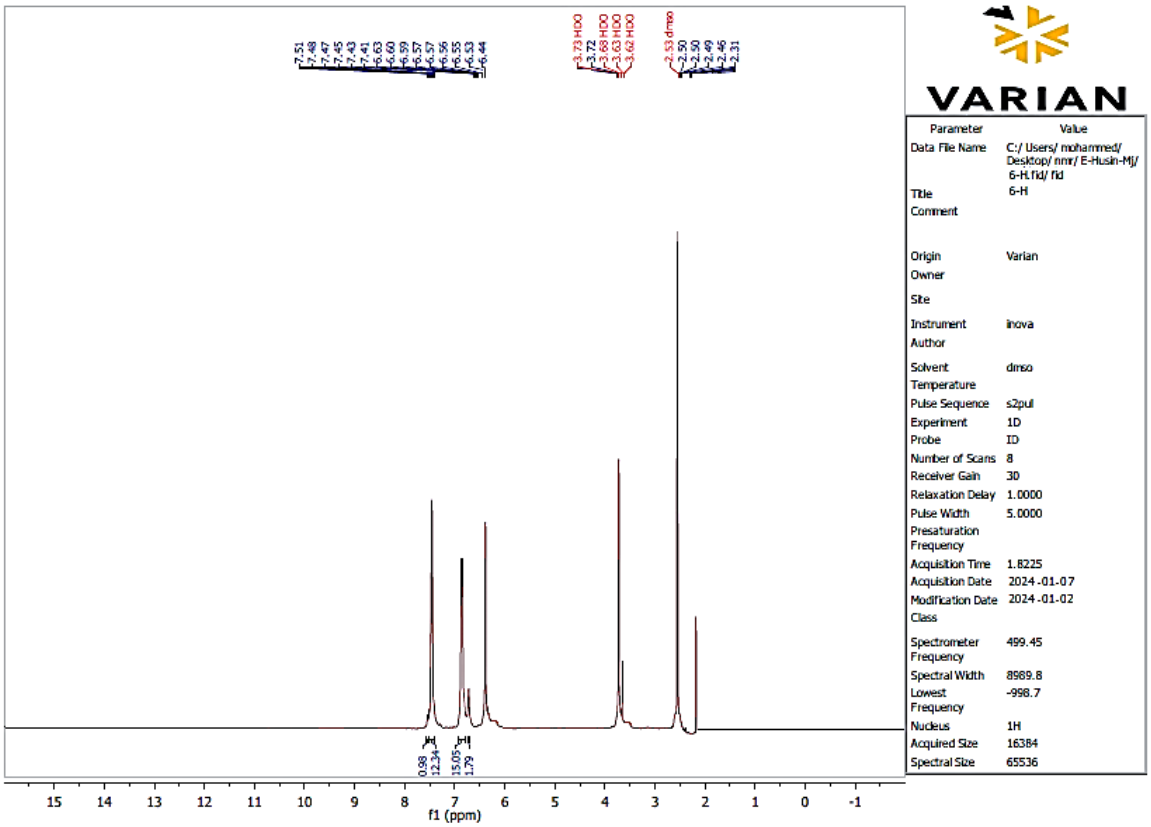

Figure 11. H.NMR-Spectrum of cycle derivative [3].

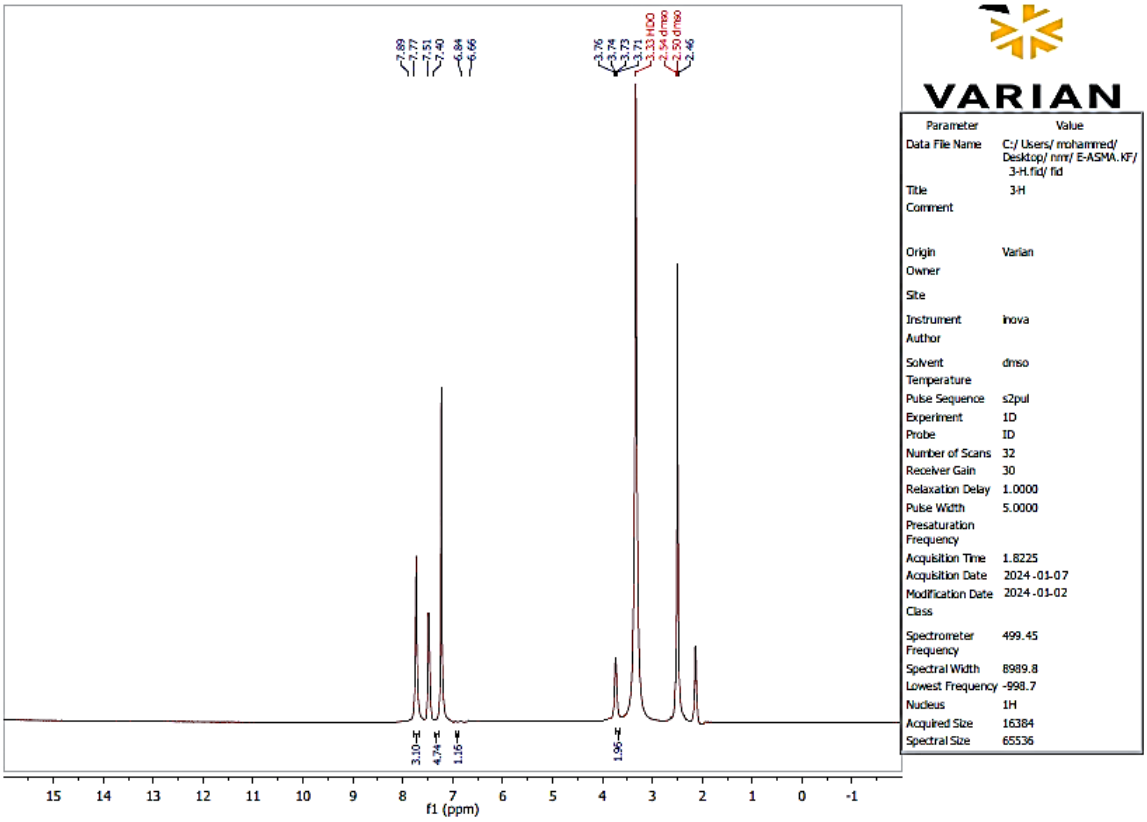

Figure 12. H.NMR-Spectrum of cycle derivative [4].

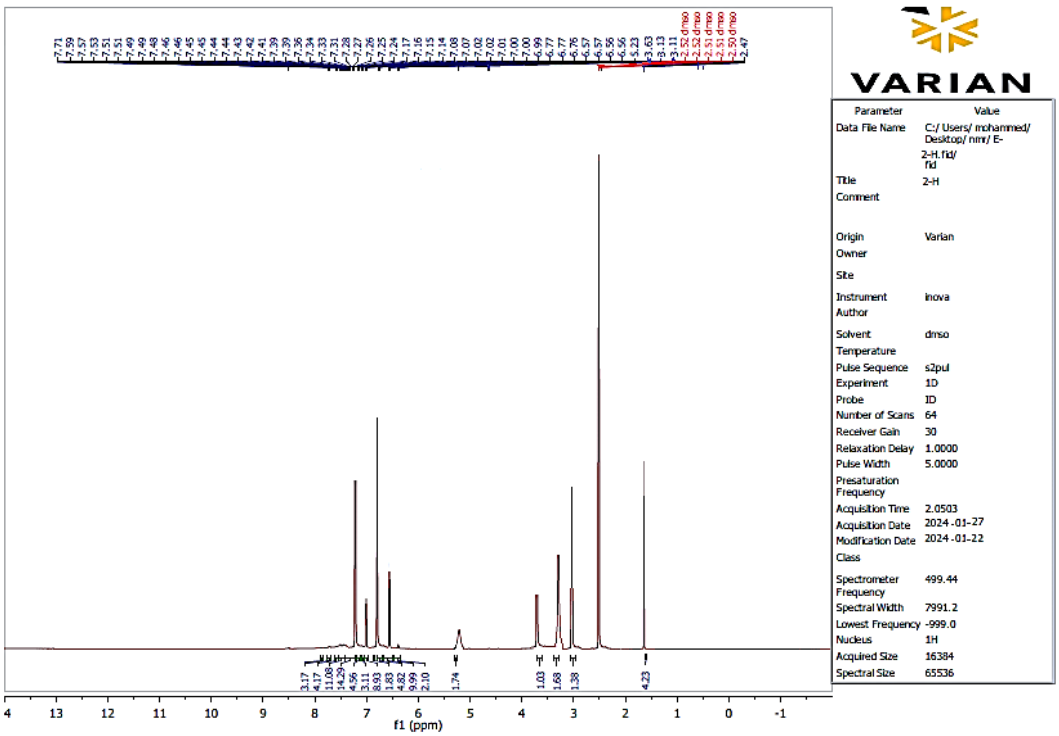

Figure 13. H.NMR-Spectrum of cycle derivative [5].

^{13}C.NMR-spectra: The characterization of derivatives by appearance peak of carbon atom carbonyl of ketone (CO-) appeared at (173.73) in compound {1} but in compound {2} the carbonyl of ketone

disappeared [43, 44] but other peak appeared for Imine group (C=N) in compound (Imine compound) that were at δ (156. 98) by flowing reference [30] as identification reference of all spectra in Figures (14–18).

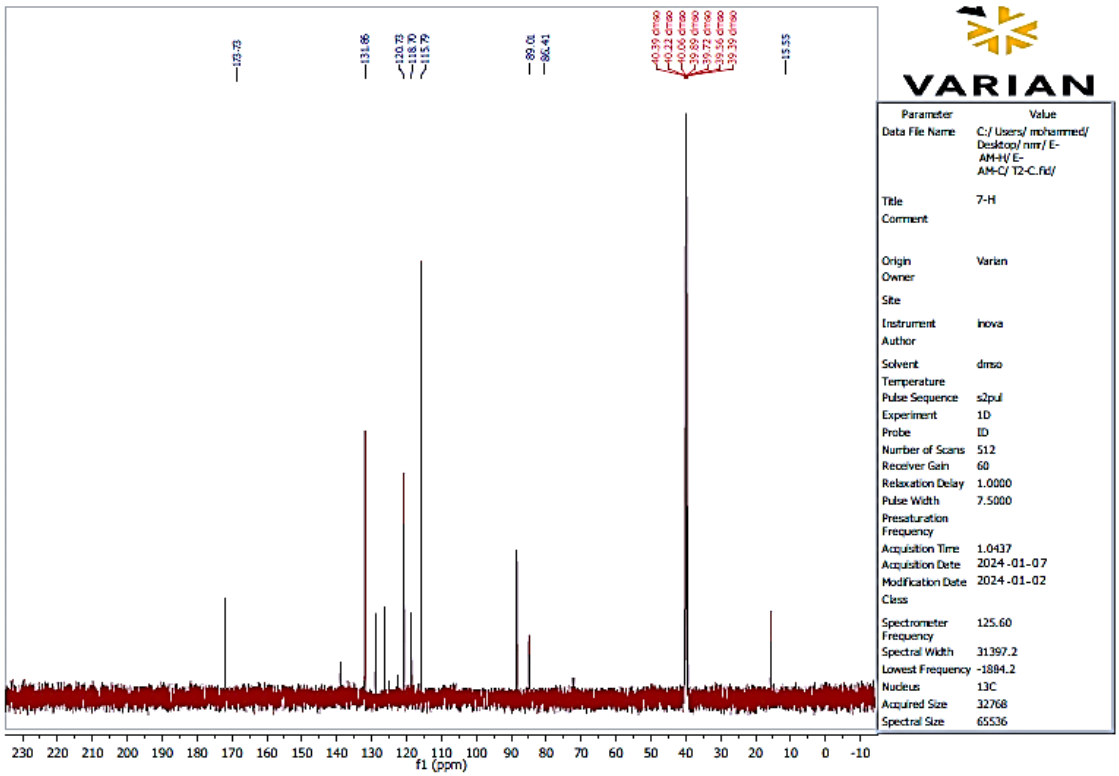

Figure 14. C.NMR-Spectrum of Azo-Derivative [1].

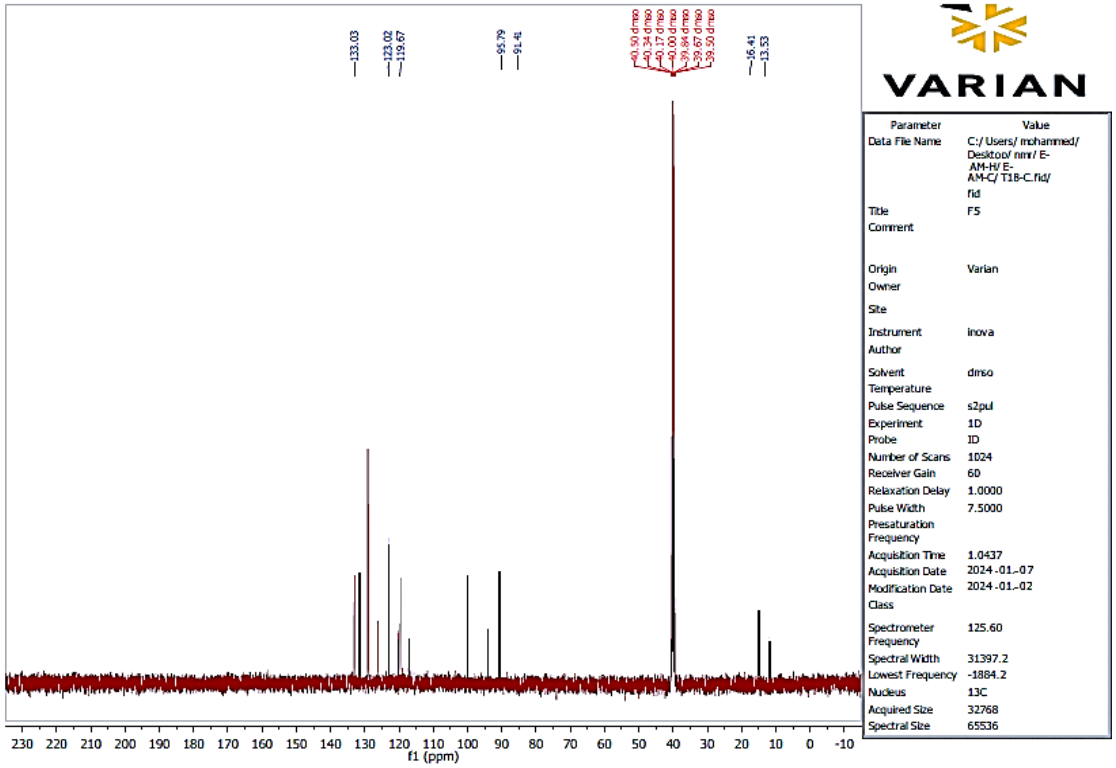

Figure 15. C.NMR-Spectrum of Azo-Anil derivative [2].

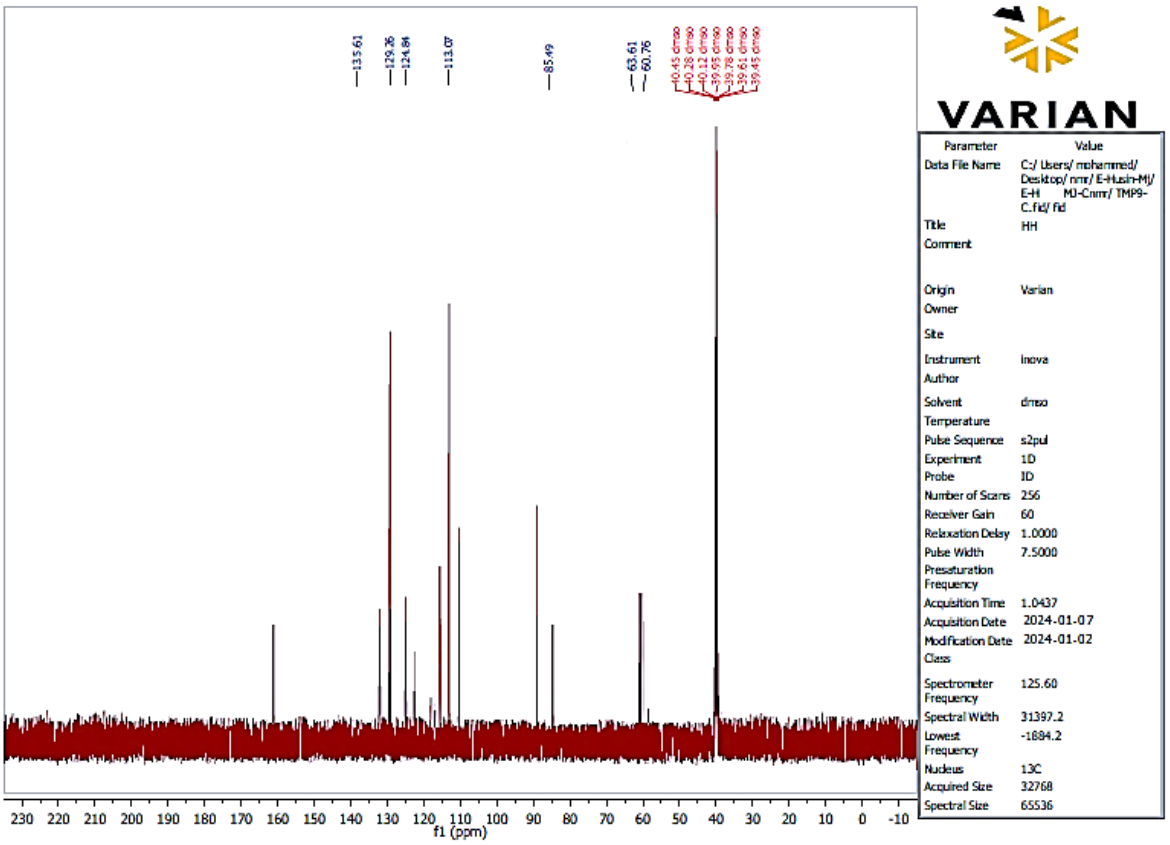

Figure 16. C.NMR-Spectrum of cycle derivative [3].

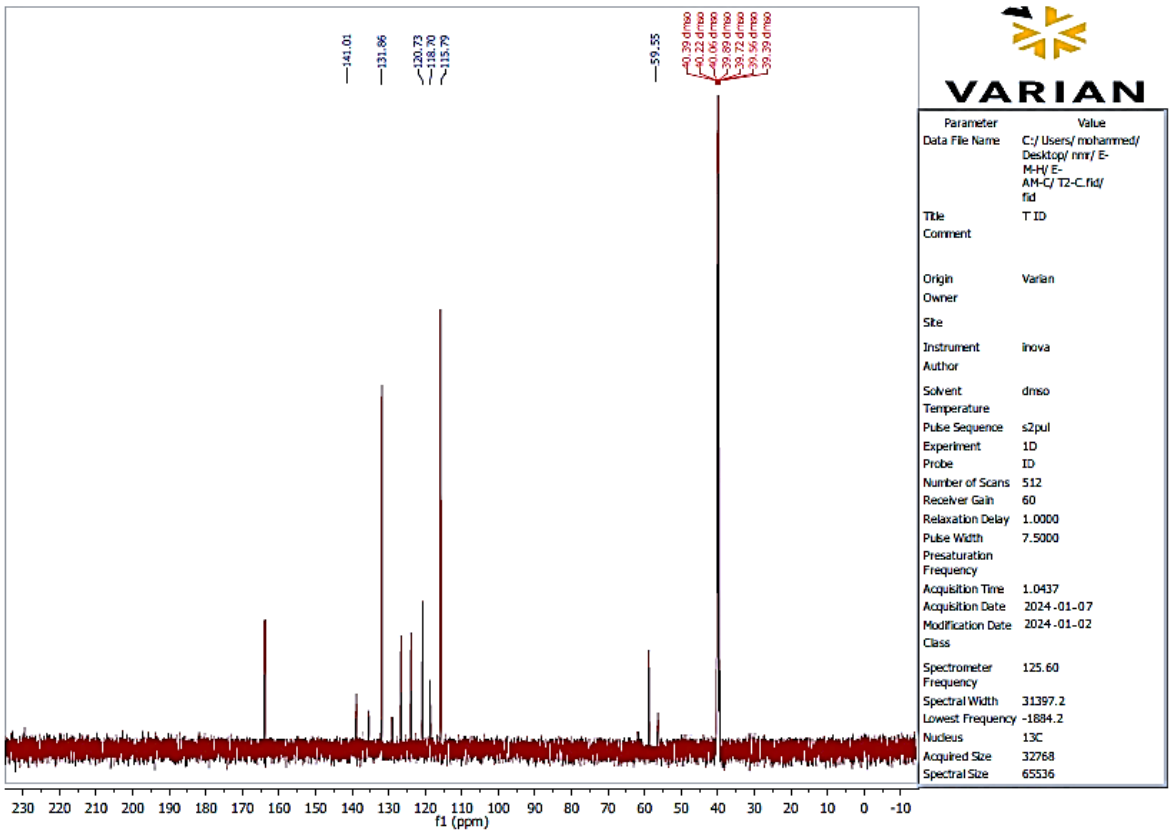

Figure 17. C.NMR-Spectrum of cycle derivative [4].

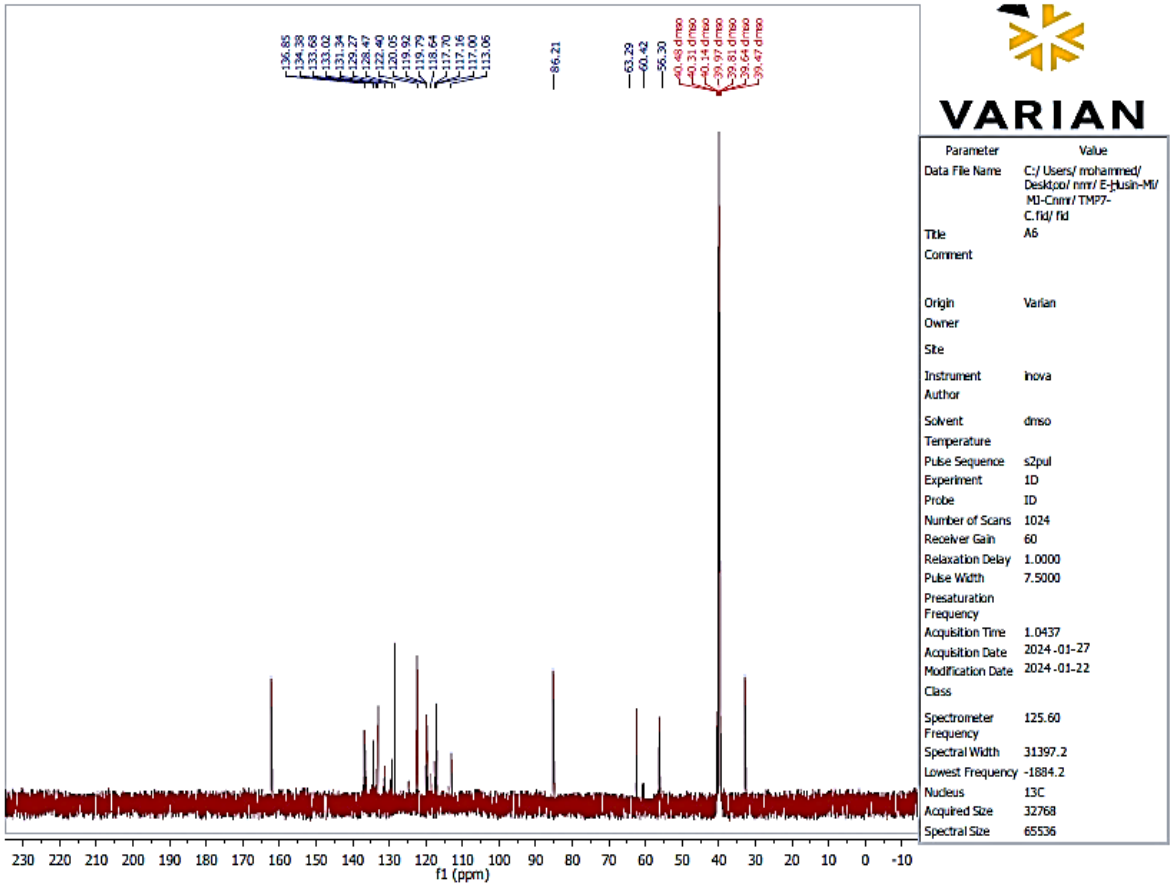

Figure 18. C.NMR-Spectrum of cycle derivative [5].

Other Characterization

All five chemical derivatives of (azo, imine and cyclic) compounds were studied to collect all the chemical and physical properties in Table 1.

Transmission-Electron Microscopy

The foundation of the study of the electron microscope comprises the use of electrons to take a picture of the samples. The source of the emission of electrons is the tungsten thread, which shoots electrons at high speed into a very thin layer of the sample, where the flow of electrons focuses on a small spot [33–36] of the sample and photographs it, then moves to another spot until it photographs all the spots formed for the sample. Radiation passes through it. The transmission electron microscope is used to study the crystal structure in terms [37–40] of the shape and size of the particles and the distribution of nanoparticle crystals, as the transmission electron microscope was used to take a picture of the shape of the crystals of compounds, where the period of compounds by the reverse sublimation methods [41–44] was two hours and under a temperature of (80º)C, according to studies [45–47]. Results of transmission electron spectroscopy of compounds {1}, {2}, {3}, {4}, and [5] after heating for 2 h have been depicted in Figures 19, 20, 21, 22 and 23, respectively.

Table 1. Additional characterization of derivatives {1–5}.

Derivatives	*P %*	*Color*	*M.P C °*	*Rf*	*Solvents (TLC)*
Comp.{1}	80	Orange	174	-----	Ethanol : Benzene
Comp.{2}	72	Yellowish Orange	196	0.62	Ethanol : Benzene
Comp.{3}	70	Reddish Orange	210	0.64	Ethanol : Benzene
Comp.{4}	78	Yellowish Orange	218	0.56	Ethanol : Benzene
Comp.{5}	70	Yellowish brown	216	0.60	Ethanol : Benzene

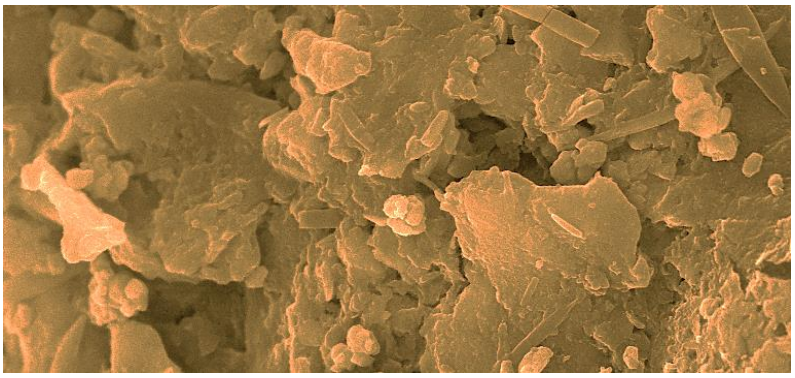

Figure 19. TEM of compound [1] at heating 2 h.

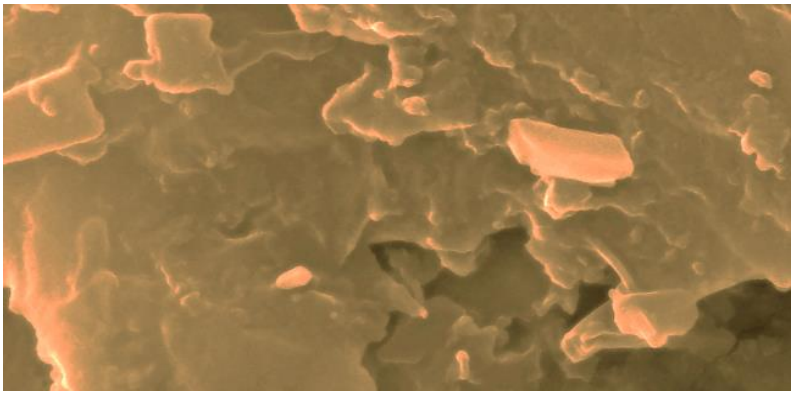

Figure 20. TEM of compound [2] at heating 2 h.

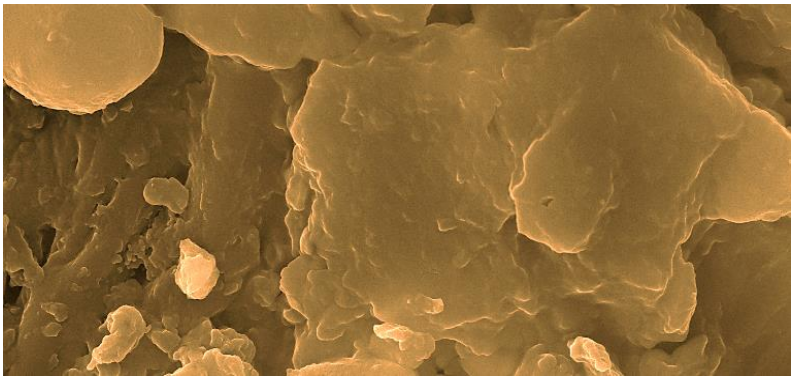

Figure 21. TEM of compound [3] at heating 2 h.

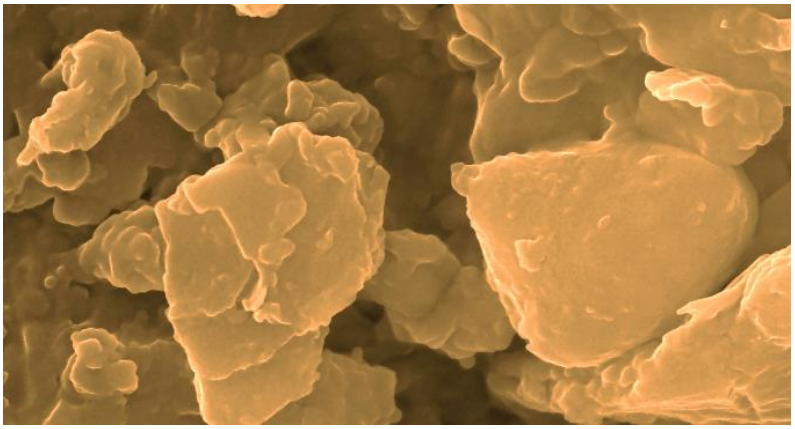

Figure 22. TEM of compound [4] at heating 2 h.

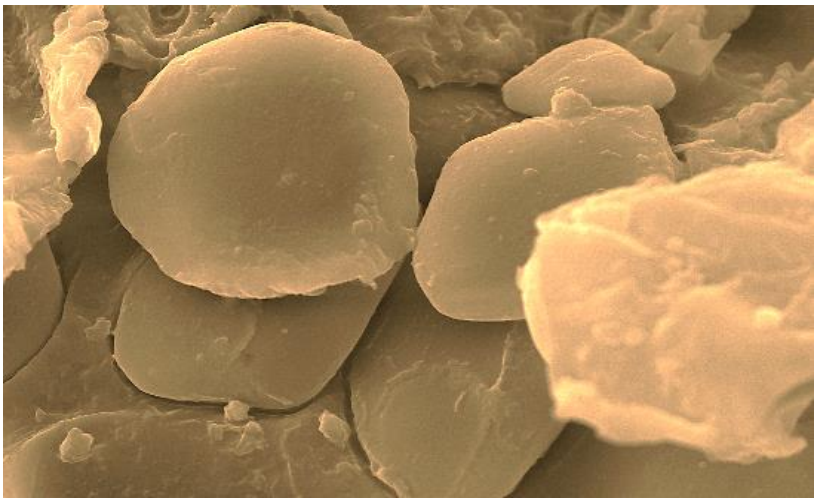

Figure 23. TEM of compound [5] at heating 2 h.

CONCLUSIONS

The nanoscale properties of organic compounds are among the most important properties for their medicinal and therapeutic applications and pharmaceutical uses. It is an important property that makes the materials it possesses able to transfer portable medications to infections present in the human body because it is small in size and has an oval shape that does not take up much space in the tissues. The prepared materials possessed this nano-structure within their composition.

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