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Synthesis and Characterization of Bisindandione Derivative Azo Dye, Experimental and Theoretical Investigation of Its Tautomeric Properties

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Abstract

In this study, the synthesis, characterization, and tautomeric properties of 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone, a new bisindandione derivative, were investigated. 2,2'-Bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone was obtained after the diazo coupling reactions between [5,5'-biindane]-1,1',3,3'-tetrone and aniline, and characterized by Fourier Transform-Infrared, proton nuclear magnetic resonance, ultraviolet-visible and mass spectroscopy. The structural and spectroscopic analyses of azo dye were examined using Density Function Theory, and vibration frequencies calculated with the optimized structure were compared with experimental data. The obtained data showed that 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone could be found in two tautomers, and the molar ratio of azo/hydrazo was found to be 0.86. The obtained data showed that the hydrazo form was dominant for 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone.

Keywords: Azo dye, DFT, tautomer.

1. Introduction

Ninhydrin has proven itself as an important analytical tool in the fields of Chemistry, Biochemistry, and Forensic Sciences since its discovery in 1910 [1]. Ninhydrin is often used in the analysis of amino acids, peptides, and proteins. In 1954, it was found to be an important reagent for fingerprint identification on porous surfaces. Ninhydrin [2], discovered by Ruhemann by chance, reacts with amines and amino acids to form the colorful compound known by the specific name Ruhemann's purple [3,4]. Ninhydrin analogs are used to obtain a highly effective amino acid reagent in forensic and analytical applications. A large number of ninhydrin analogs have been synthesized through the extension of the conjugated system, insertion of various substituents, and improvements to have a fluorescence effect. These analogs usually involve oxidation of 1-indanone or 1,3-indandions [5]. 1,3-indandione and its derivatives used as the starting reagent for the synthesis of many important compounds is used in many fields of science and technology, such as drug synthesis [6], forensic chemistry for fingerprint detection [7], dyes and pigments [8-10], semi- and photo-conductors [11], and synthesis of non-linear optical materials [12]. Furthermore, the synthesis of different derivatives, the preparation of complexes, the examination of their theoretical properties, as well as, the investigation of their antimicrobial effects have taken place in the literature [13-18]. Although the [5,5'-Biindandion]-1,1',3,3'-tetron, a bisindandione compound, was first synthesized by Ozolina and Neilina in 1971, no another study on this compound has been encountered in the literature [19].

Azo dye is a large π conjugated molecular system. Azo dye molecules, electron-giving (D), and electron-accepting groups (A) are bound by a π conjugate binder (D-π-A molecular structure). Azo dyes with D-π-A chromosphere system have large π systems located along with the azo bonding between the receiver and donor units. Azo dyes are a class of colorants that are widely used in many areas, from textiles to non-textile applications [20,21]. Numerous studies have been reported that they are used in various fields such as dyeing textile fibres, coloring various materials, colored plastics and polymers, biological-medical studies and advanced applications in organic synthesis [22-28].

In this study, 3,3',4,4'-biphenyltetracarboxylic acid tetramethyl ester was synthesized by reacting with methanol and 3,3',4,4'-biphenyltetracarboxylic dianhydride in the acidic medium. This compound was reacted with freshly prepared sodium sand and ethyl acetate and a compound of [5,5'-biindane]-1,1',3,3'-tetrone was obtained. Subsequently, using aniline as a diazonium component, a new disperse azo dye, 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone compound was obtained via diazonium bonding reaction (Figure 1). The structure of the compound was illuminated by determining its characterization. Experimental findings were compared with theoretical results.

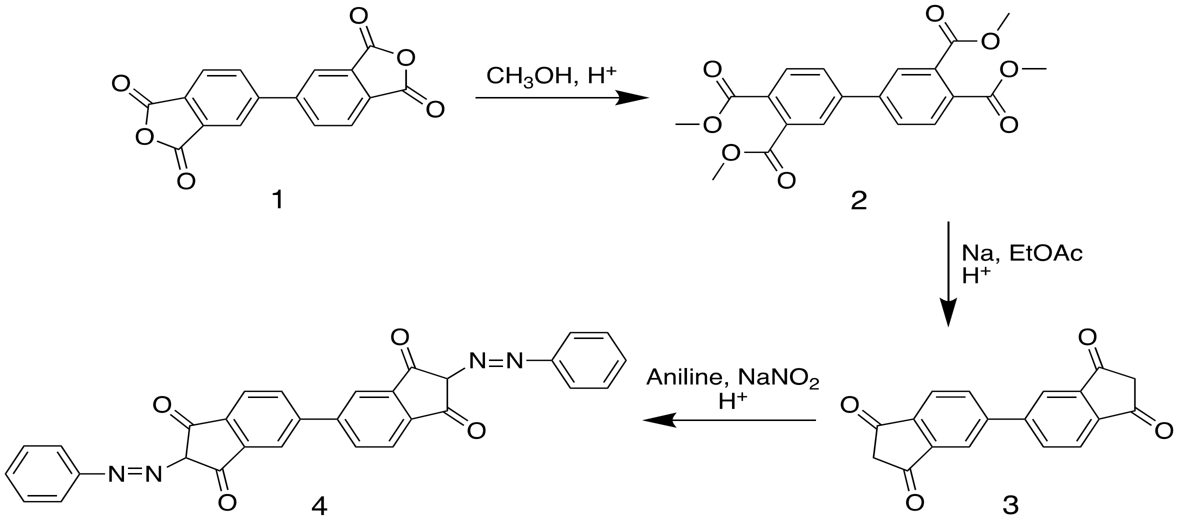

Figure 1. Synthesis of 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone.

2. Experimental

2.1. Materials and Methods

3,3',4,4'-Biphenyltetracarboxylic dianhydride (**1**, 97%, Sigma-Aldrich), sodium (99.9%, Sigma-Aldrich), *p*-xylene (≥99%, Sigma-Aldrich), sodium nitrite (≥97%, Sigma-Aldrich), sodium hydroxide (≥98%, Sigma), methanol (≥99.9%, Sigma-Aldrich), ethyl acetate (99.8%, Sigma-Aldrich), aniline (≥99.5%, Sigma-Aldrich) and ethanol (≥99.8%, Sigma-Aldrich) were used as received without further purification. Infrared spectra were recorded using KBr in the Mattson 1000 Fourier Transform Infrared (FTIR) spectroscopy. Bruker Spectrospin Avance DTX 400 Ultra-Shield was used in DMSO-d_6 for proton nuclear magnetic resonance (^{1}H NMR) spectrometry, and Agilent 1100 MSD was used for mass spectrometry (MS). The ultraviolet-visible (UV-Vis) absorption spectra were measured on a Unicam UV2-100 spectrophotometer at the wavelength of maximum absorption in a range of solvents, including DMSO, DMF, methanol, acetonitrile, acetic acid and chloroform.

2.2. Synthesis

2.2.1. Synthesis of tetramethyl ester of 3,3',4,4'-biphenyltetracarboxyl acid (2)

3,3',4,4'-Biphenyltetracarboxylic dianhydride (**1**) (0.02 mol, 5.88 g) was taken into a 250 mL volumetric flask and heated under a condenser after 50 mL methanol added. At the end of 1 hour, the product, followed by thin-layer chromatography, was cooled at room temperature and 5 mL of the prepared with methanol was added with the help of separating funnel. The product was heated again for 4 hours under the condenser. At the end of the reaction, the product was cooled and poured into ice water. It was filtered and dried. It was purified by column chromatography using chloroform as eluent. Yield 80%, mp 95-97 °C.

2.2.2. Synthesis of [5,5'-biindane]-1,1',3,3'-tetron (3)

Sodium metal (1.22 g, 0.053 mol) was taken into a volumetric flask. It was heated under condenser in dry *p*-xylene. The sodium was melted and cooled. It was shaken to make sodium sand completely. Freshly prepared sodium sand was taken into a 250 mL volumetric flask. Then, **2** (0.013 mol, 5.12 g), 30 mL of ethyl acetate and 1 mL of methanol were added the flask. The red-colored mixture was heated under the condenser for 8 hours. Dark yellow precipitates were observed to form during the reaction. Then, 5 mL of ethanol was added on it, and the product was filtered. Obtained diethyl 1,1',3,3'-tetraoxo-[5,5'-biindan]-2.2'-dicarboxylate disodium salt was acidified with 10% H_2SO_4, cooled, filtered, and green-colored product was obtained. Yield 89%.

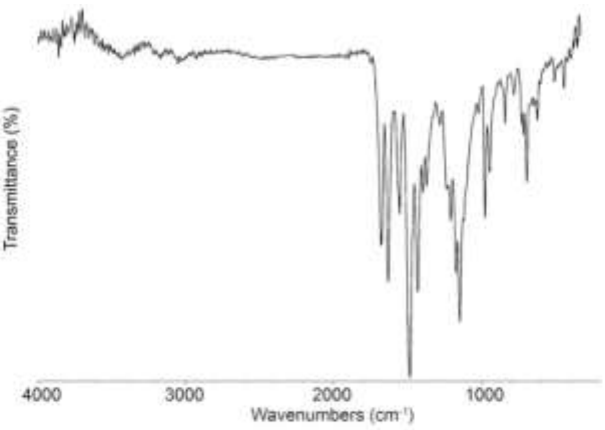

Figure 2. Experimental FTIR spectrum of the 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone.

2.2.3. Synthesis of 2,2'-Bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone (4)

Aniline (2 eq, 0.004 mol, 0.37 g) was dissolved in 5 mL of deionized water. Then, 4 mL of 36% HCl solution was added and cooled with ice bath. Sodium nitrite (2 eq, 0.004 mol, 0.28 g), which was dissolved in 5 mL of water, was added into the reaction mixture drop by drop. This prepared cold diazonium salt was added onto [5,5'-biindan]-1.1',3,3'-tetrone (**3**) (1 eq, 0.002 mol, 0.57 g), which is dissolved in dilute NaOH solution. Then pH was set to 8-9. It was mixed for 3 hours at room temperature, acidified, filtered, and crystallized with dimethyl sulfoxide. Yield 81%, mp: 243°C decomposition.

2.3. Theoretical Calculations

Density function theory calculations were performed using Gaussian 09W software [29], and molecular geometry was visualized with GaussView 5.0.9 [30]. The molecular structure of the 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone compound was calculated using the DFT/B3LYP [31] method and the 6-31g(d) basis set. With the resulting optimized structure, vibration frequencies were calculated using DFT/B3LYP method.

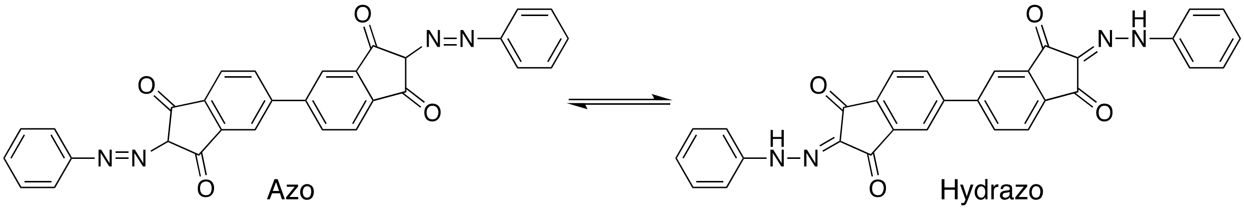

Figure 3. Tautomers of 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone compound.

3. Results and Discussion

Synthesis of 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone was performed in three steps, and the products obtained in each step were purified, and their yield were calculated. In the last step, 89% yield was obtained from 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone as a result of diazonium coupling reaction between [5,5'-biindane]-1.1', 3,3'-tetrone and aniline. FTIR, ^{1}H NMR, UV-Vis and MS were used for the characterization of the resulting 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone compound.

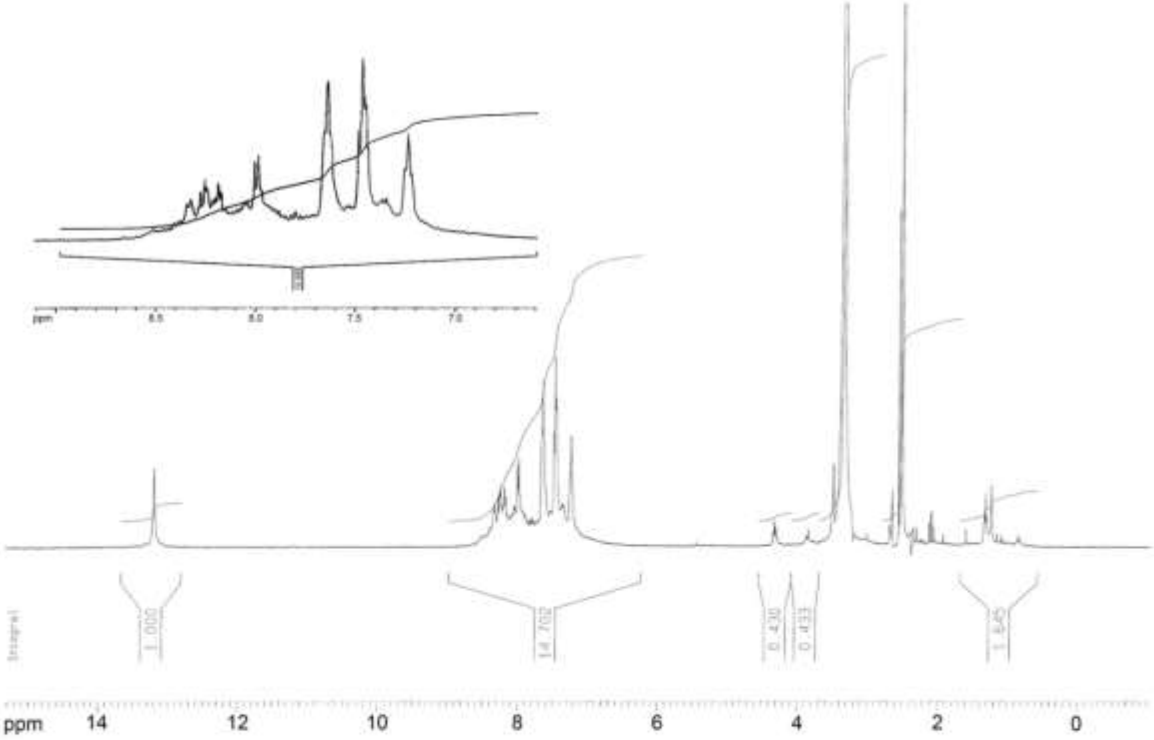

Figure 4. Experimental ^{1}H NMR spectrum of the 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone.

Figure 2 shows the FTIR spectra of 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone in the wavenumber region 4000-525 cm^{-1}. As seen, the absorption bands of azo dye appeared at around 3123, 1712 and 1660 cm^{-1} corresponding to the aromatic C-H, C=O and C=N stretching, respectively. The azo dye was characterized by the presence of the absorption band at 1560-1480 cm^{-1} assigned to N=N vibration [32]. At the same time, the presence of a weak band address to the N-H stretching at ~3200 cm^{-1} was determined. Azo dyes can be found in two possible tautomeric structures as azo and hydrazo (Figure 3). The bands of the N-H and C=N stretch observed at ~3200 and 1660 cm^{-1}, and the peaks of the N=N stretch indicate that the hydrazo and azo tautomers of the structure are together.

The ^{1}H-NMR spectrum of the 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone in DMSO-d_6 is given in Figure 4. The aromatic protons were observed between 8.34 and 7.22 ppm. Two protons for azo form were observed at 4.31 and 3.89 ppm. However, hydrazo forms had two protons (N-H), and they were observed at 13.3 ppm. This result confirmed the FTIR results. The azo/hydrazo ratio was calculated by integrating the peak ratio of the characteristic chemical shifts (δ) corresponding to the azo and hydrazo by using the MestReNova v12.0.3. The integration of the characteristic peaks associated with azo (4.31-3.89 ppm) and hydrazo (13.3 ppm) were used to make the calculations. The molar ratio of azo/hydrazo was found to be 0.86. It was concluded that the hydrazo form is dominant for the 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone. The mass of the 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone compound ($C_{30}H_{18}N_4O_4$ m/z) was determined to be 498.40. The result is compatible with the theoretical (498.13) data.

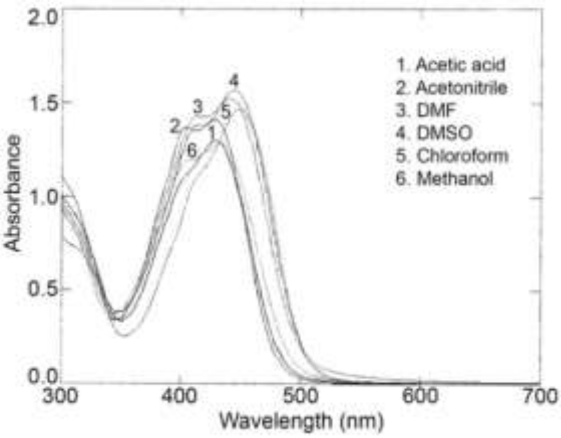

Figure 5. Absorption spectra of 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone in various solvents.

The UV-Vis absorption spectra of the 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone were recorded between 300-700 nm using a variety of solvents, and the results are shown in Figure 5. The absorption maxima of the dye were found to be independent of the solution phase and did not correlate with the dielectric constants of the solvents. 2,2'-Bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone showed absorption maxima at 445 nm in DMSO, 441 nm in DMF, 433 nm in acetonitrile, 433 nm in methanol, 434 nm in acetic acid, and 445 nm in chloroform. There were no significant differences observed for absorption maxima. On the other hand, 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone showed a maxima absorption peak with a shoulder in all solvents. It suggests that 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone could be found in two tautomers. This result confirmed FTIR and ^{1}H-NMR results.

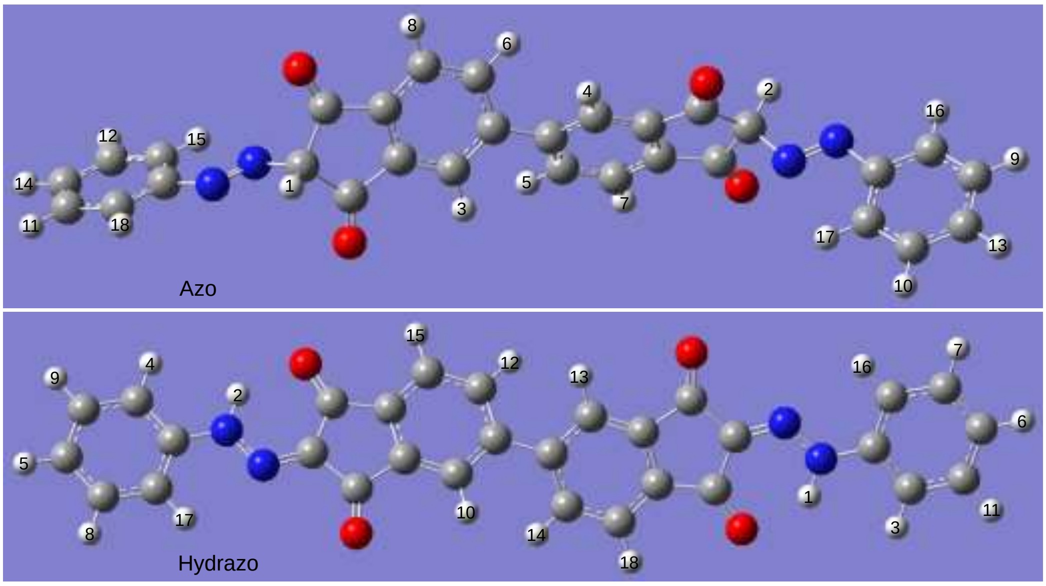

Figure 6. Optimized structures of azo and hydrazo forms of 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone.

Table 1. The total energies calculated for the azo and hydrazo structures of the 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone (E).

Tautomer	**Total energy (a.u.)**
Azo	-1673.84466610
Hydrazo	-1673.90499867

As mentioned above, azo dyes can be found in two possible tautomeric structures as azo and hydrazo. For both structures, the optimized structures obtained using the DFT/B3LYP method and the 6-31g(d) basis set are given in Figure 6. The total energies of azo and hydrazo structures were calculated using optimized structures and given in Table 1. When the calculated total energies were examined, it was determined that the hydrazo form for the compound 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone was more stable. When the two tautomeric structures were examined, they were determined to be longer than the theoretical value (1.252 Å [33]) of diazene (HN=NH) bond length. The N=N bond length of azo form was determined to be 1.40 Å due to steric effects, while to be 1.2529 Å in the hydrazo structure.

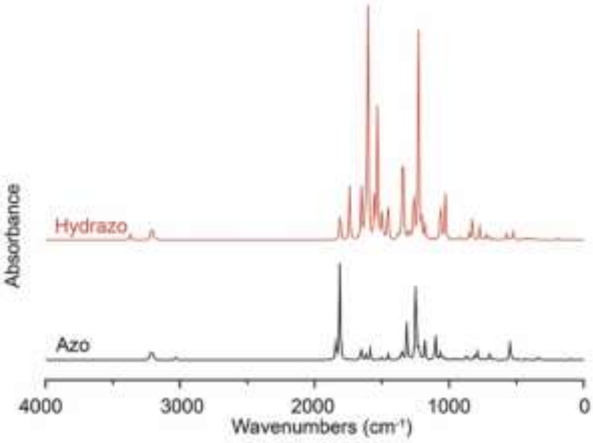

Figure 7. Theoretical FTIR spectra of 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone compound.

The stable form of hydrazo was used in the calculation of the vibrational frequencies of the synthesized compound. Figure 7 contains the theoretical FTIR spectra for both tautomers of the 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone compound. The wavenumbers calculated for the groups of -N-H and C=O were determined as 3368 cm^{-1} and 1810-1738 cm^{-1}, respectively. Compared to theoretical results, it shows that experimental results shift to a lower wavenumber of about 50-100 cm^{-1}. This lower shift makes it clear that strong hydrogen bonds are formed between the -N-H and C=O groups [22]. However, when the FTIR spectrum of azo form was examined, the characteristic band of N=N group was observed at 1588 cm^{-1}. However, no bands were identified resulting from -N-H stretch. ^1H NMR spectra were obtained using the Gauge-including atomic orbital (GIAO) method given in Figure 6 for both optimized structures. Aromatic protons were observed between 8.3-7.0 ppm for both tautomers. Chemical shift values of protons in the ring to which carbonyl groups are attached in the azo

Table 2. Theoretical ^1H NMR data of azo and hydrazo forms of 2,2'-Bis(fenilazo)-5,5'-biindan-1,1',3,3'-tetrone.

Protons	**Tautomer**	
	Azo (ppm)	**Hydrazo (ppm)**
$H_{1Hydrazo}$	-	15.0059
$H_{2Hydrazo}$	-	14.9247
H_3	8.9224	8.2765
H_4	8.9106	8.2577
H_5	8.8158	8.2531
H_6	8.8050	8.2373
H_7	8.7376	8.1791
H_8	8.7333	8.1774
H_9	8.1367	8.0855
H_{10}	8.1311	8.0682
H_{11}	8.1023	8.0638
H_{12}	8.0570	8.0583
H_{13}	8.0432	8.0571
H_{14}	8.0158	8.0444
H_{15}	7.9681	8.0250
H_{16}	7.8655	8.0231
H_{17}	7.8583	8.0205
H_{18}	7.6393	8.0108
H_{1Azo}	5.9705	-
H_{2Azo}	5.5374	-

structure were calculated as 6.0-5.5 ppm. Protons belonging to hydrazo form (N-H) were observed in the range of 15.0-14.9 ppm, but no peak was observed in this region in the azo form. Theoretical ^{1}H NMR data for azo and hydrazo structures are given in Table 2.

4. Conclusion

In this study, synthesis and characterization of 2,2'-bis(phenylazo)-5,5'-biindane-1,1',3,3'-tetrone, a new bisindandione derivative, were performed. First, the compound **2** was obtained as a result of the reaction of the compound **1** with methanol in acidic medium, then, followed by the reaction with freshly prepared sodium sand and ethylacetate, compound **3** was obtained. At the last step, the synthesis of azo dye (**4**) was synthesized with 81% yield via a coupling reaction. The synthesized compound was characterized by FTIR, ^{1}H NMR, UV-Vis and MS. As a result of experimental and theoretical studies, it was determined that the hydrazo form of bisindandione derivatives was more stable than the azo form.

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