Gazi Üniversitesi
Fen Bilimleri Dergisi
PART C: TASARIM VE TEKNOLOJİ

Gazi University
Journal of Science
PART C: DESIGN AND TECHNOLOGY

GU J Sci, Part C, 11(3): 727-734 (2023)

Structure and Spectroscopic Studies of Bis Azo Compounds with S/SO$_2$ Bridges and Containing Cyclic-1,3-Dicarbonyl Groups

Gülnihal ERTEN[1*], Naki ÇOLAK[1]

[1]*Hitit University, Faculty of Science and Art, Department of Chemistry, Çorum Turkey*

Article Info

Research article
Received: 18/04/2023
Revision: 13/07/2023
Accepted: 14/07/2023

Keywords

Bis azo dyes
Spectroscopic studies
Dimedone
Tautomerism

Makale Bilgisi

Araştırma makalesi
Başvuru: 18/04/2023
Düzeltme: 13/07/2023
Kabul: 14/07/2023

Anahtar Kelimeler

Bis azo boyalar
Spektroskopik çalışmalar
Dimedon
Tautomerizm

Graphical/Tabular Abstract (Grafik Özet)

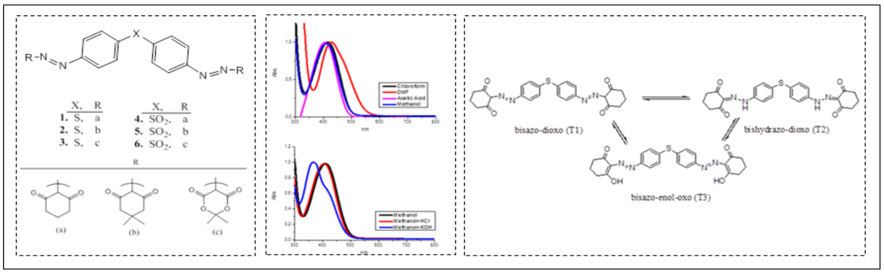

***Figure A**: Bis azo compounds (1-6) containing S/SO$_2$ and cyclic-1,3-dicarbonyl groups / **Şekil A:** S/SO2 ve siklik-1,3-dikarbonil grupları içeren bis azo bileşikler (1-6)*

Highlights (Önemli noktalar)

- *Six new bis azo dyes with S/SO$_2$ bridge containing cyclic-1,3-dicarbonyl groups were obtained from dianiline derivatives. / Dianiline türevlerinden siklik-1,3-dikarbonil grupları içeren S/SO$_2$ köprülü altı yeni bis azo boyası elde edilmiştir.*
- *The structure of the bis azo dyes was investigated by using, FT-IR, ^{1}H-NMR, LC–MS/MS and UV–Visible spectrophotometric methods. / Bis azo boyalarının yapısı FT-IR, ^{1}H-NMR, LC–MS/MS ve UV–Visible spektrofotometrik yöntemler kullanılarak incelenmiştir.*
- *UV visible absorption spectra of bis azo dyes were investigated in different solvents and also in inorganic acidic-basic media. / Bis azo boyaların UV görünür absorpsiyon spektrumları, farklı çözücülerde ve ayrıca inorganik asidik-bazlı ortamda incelenmiştir.*

Aim (Amaç): *This study, it is aimed to synthesize new bis azo dyes that can be used in synthetic fibre dyeing and to obtain more bathochromic colours and higher tinctorial effect. / Bu çalışmada, sentetik elyaf boyamada kullanılabilecek yeni bis azo boyalarının sentezlenmesi ve daha batokromik renkler ve yüksek renklendirme etkisi elde edilmesi amaçlanmıştır.*

Originality (Özgünlük): *In our study, original bis azo dyes with biologically active and high tincture properties were brought to the literature by combining the two active compounds, S/SO$_2$ dianiline derivatives and cyclic-1,3-dicarbonyl groups, using the diazo-coupling method. / Çalışmamızda iki aktif bileşik olan S/SO$_2$ dianilin türevleri ve siklik-1,3-dikarbonil grupları diazo-eşleştirme yöntemi kullanılarak birleştirilerek biyolojik olarak aktif ve renklendirme özelliği yüksek orijinal bis azo boyalar literatüre kazandırılmıştır.*

Results (Bulgular): *Three tautomeric forms bis azo-dioxo (T1), bis hydrazo-dioxo (T2) and bis azo-enol-oxo (T3) were estimated for bis azo dyes regarding present FT-IR and ^{1}H-NMR data. According to the UV-Vis spectrum, it was observed a single maximum absorption peak in all solvents. / Bis azo-diokso (T1), bis hidrazo-diokso (T2) ve bis azo-enol-okso (T3) olmak üzere üç tautomerik form, mevcut FT-IR ve ^{1}H-NMR verilerine göre bis azo boyaları için tahmin edilmiştir. UV-Vis spektrumuna göre, tüm çözücülerde tek bir maksimum absorpsiyon zirvesi gözlendi.*

Conclusion (Sonuç): *In the ^{1}H-NMR Spectrum, we can say that our compounds are in bishydrazo-dioxo form. It has been observed generally that bis azo dyes containing the sulfonyl group have a more low wavelength as against the sulfo group in all solutions. According to the absorption data the compounds are thought to be mostly in the bis hidrazo-dioxo (T2) tautomeric form in the solution medium. The observed wavelength shouldering in basic medium shows that two different tautomeric forms coexist in the basic environment of dye solutions. / ^{1}H-NMR Spektrumunda bileşiklerimizin bishidrazo-diokso formunda olduğunu söyleyebiliriz. Genel olarak tüm çözeltilerde sülfonil grubu içeren bis azo boyalarının sülfo grubuna göre daha düşük dalga boyuna sahip olduğu gözlenmiştir. Absorpsiyon verilerine göre bileşiklerin çözelti ortamında çoğunlukla bis hidrazo-diokso (T2) tautomerik formda olduğu düşünülmektedir. Bazik ortamda gözlenen dalga boyu omuzlaması, boya çözeltilerinin bazik ortamında iki farklı tautomerik formun bir arada var olduğunu göstermektedir.*

---

*Corresponding author, e-mail: gulnihaldavulgaerten@gmail.com

DOI: 10.29109/gujsc.1285026

GU J Sci, Part C, 11(3): 727-734 (2023)

Gazi Üniversitesi
Fen Bilimleri Dergisi
PART C: TASARIM VE TEKNOLOJİ

Gazi University
Journal of Science
PART C: DESIGN AND TECHNOLOGY

http://dergipark.gov.tr/gujsc

Structure and Spectroscopic Studies of Bis Azo Compounds with S/SO_2 Bridges and Containing Cyclic-1,3-Dicarbonyl Groups

Gülnihal ERTEN[1*], Naki ÇOLAK[1]

[1]*Hitit University, Faculty of Science and Art, Department of Chemistry, Çorum Turkey*

Article Info

Research article
Received: 18/04/2023
Revision: 13/07/2023
Accepted: 14/07/2023

Keywords

Bis azo dyes
Spectroscopic studies
Dimedone
Tautomerism

Abstract

A sequence of new bis azo dyes was synthesized using aromatic diamines with S/SO_2 bridges and cyclic-1,3-dicarbonyl compounds containing active methylene groups; 3,3-dimethyl-1,5-cyclohexadione (dimedone), 1,3-cyclohexadione and 2,2-dimethyl-1,3-dioxane-4,6-dione, and was obtained dyes **1-6**. Whether the reaction was complete and the purity of the compounds was controlled with TLC. The structure of the newly synthesized compounds was investigated by using, FT-IR, ^{1}H-NMR, LC–MS/MS and UV–Visible spectrophotometric methods, CH_3OH was used in the LC-MS/MS experiments, and the molecular masses of the compounds were seen as M and M^{+1} protonated in the spectrum. In the absorption spectra of these compounds, the solvent effect by using different solvents and also the acid-base effect by adding HCl or KOH to the medium were investigated. The tautomeric equilibrium forms (enol-imine O-H….N, keto-amine O….H-N forms) of the compounds were investigated according to the electronic spectrum recorded in chloroform, dimethylformamide (DMF), acetic acid and methanol solvents. The results of the UV-visible and ^{1}H-NMR spectra indicated that the compounds in chloroform, dimethylformamide (DMF), acetic acid and methanol were found in the hydrazo tautomer (keto-amine O….H-N forms) of the proposed tautomeric forms.

S/SO_2 Köprülü ve Siklik-1,3-Dikarbonil Grupları İçeren Bis Azo Bileşiklerinin Yapısı ve Spektroskopik Çalışmaları

Makale Bilgisi

Araştırma makalesi
Başvuru: 18/04/2023
Düzeltme: 13/07/2023
Kabul: 14/07/2023

Anahtar Kelimeler

Bis azo boyalar
Spektroskopik çalışmalar
Dimedon
Tautomerizm

Öz

S/SO_2 köprülü aromatik diaminler ve aktif metilen grupları içeren siklik-1,3-dikarbonil bileşikleri; 3,3-dimetil-1,5-siklohekzadion (dimedon), 1,3-siklohekzadion ve 2,2-dimetil-1,3-dioksan-4,6-dion kullanılarak bir dizi yeni bis azo boyası sentezlendi ve 1-6 boyaları elde edildi. Reaksiyonun tamamlanıp tamamlanmadığı ve bileşiklerin saflığı TLC ile kontrol edildi. Yeni sentezlenen bileşiklerin yapısı, FT-IR, ^{1}H-NMR, LC-MS/MS ve UV-Visible spektrofotometrik yöntemler kullanılarak incelenmiş, LC-MS/MS deneylerinde CH_3OH kullanılmış ve bileşiklerin molekül kütleleri spektrumda protonlanmış M ve M^{+1} olarak görüldü. Bu bileşiklerin absorpsiyon spektrumlarında farklı çözücüler kullanılarak çözücü etkisi ve ortama HCI veya KOH eklenerek asit-baz etkisi de incelenmiştir. Bileşiklerin tautomerik denge formları (enol-imin O-H….N, keto-amin O….H-N formları), kloroform, dimetilformamid (DMF), asetik asit ve metanol çözücülerinde kaydedilen elektronik spektruma göre incelenmiştir. UV-görünür ve ^{1}H-NMR spektrumlarının sonuçları, kloroform, dimetilformamid (DMF), asetik asit ve metanoldeki bileşiklerin önerilen tatomerik formların hidrazo tautomerinde (keto-amin O….H-N formları) bulunduğunu gösterdi.

1. INTRODUCTION (GİRİŞ)

Aromatic diazonium compounds, which are very unstable structures, must give a coupling reaction with a nucleophile immediately after their synthesis, for this purpose active methylene groups can be used [1–3]. As a consequence of reactions among primary amines and active methylene groups, products known in organic chemistry as diazonium groups are formed. These compounds exhibit different fastness and tinctorial properties according to the chemical structure of the diazo component and the coupling component. It is known that carbocyclic azo dyes have weaker tinctorial

---

*Corresponding author, e-mail: gulnihaldavulgaerten@gmail.com

DOI: 10.29109/gujsc.1285026

properties compared to heterocyclic azo dyes [4]. In our study, we aimed to design bis azo dyes containing carbocyclic structures with better tinctorial properties.

Cyclohexane, cyclohexanol, and cyclohexanone azo dyes are utilized as preliminary compounds in the medicinal and chemical industries. Cyclohexanol and cyclohexanone used as intermediates for a lot of organic compounds (pharmaceutical agents, rubber or pesticide chemicals, etc.) are obtained from cyclohexane [5]. Dimedone is an active methylene component, therefore it gives easy coupling with diazonium salts and high enolization in the azo-coupling reaction. Brightly colorful hydrazones can be obtained by azo-coupling reactions [6]. As typical reactive 1,3-dicarbonyl compounds, cyclohexane-1,3-dione, and its analogies 5,5-dimethyl cyclohexane-1,3- dione (dimedone) and 2,2-dimethyl-1,3-dioxane-4,6-dione have been widely used in versatile synthetic reactions. The use of cyclic-1,3-dicarbonyls, which have significant synthetic potential reactions, as coupling components in azo compounds has also been documented [7]. Azo derivatives of cyclic-1,3-diketones are of great importance in fundamental and applied studies [8-10]. Azo dyes are of potential biological activities such as antifungal [11-17], antimycobacterial [18], antibacterial [19], anticancer-chemotherapy [20-22], anti-HIV [23–28], DNA-cleavage [29] and in the textile, food and cosmetics industry [30-32]. Azo dyes are interesting compounds that can be used in many applications due to their colors and different properties [33-34].

In this study, a series of bis azo dyes based on dianiline derivatives including 1,3-dicarbonyl groups, such as cyclohexane-1,3-dione, 5,5-dimethyl cyclohexane-1,3- dione (dimedone) and 2,2-dimethyl-1,3-dioxane-4,6-dione, were synthesized and investigated solvatochromic behaviors of these bis azo dyes on UV-Vis spectra.

2. MATERIALS AND METHODS (MATERYAL VE METOD)

2.1. Experimental Equipment (Deneysel Ekipman)

All chemicals purchased with Merck and Aldrich chemical companies were used with no purification. Melting points were determined on a Stuart-SMP30 instrument with the capillary tube and were not corrected. Thermo Nicolet 6700 FT-IR spectrometer (on ATR) at Hitit University was used for infrared spectra (4000-400 cm-1). Brucker Avance DPX-400 NMR device (solvent $CDCl_3$; internal standard TMS) at Fırat University was used for proton nuclear magnetic resonance (^{1}H-NMR) spectra. LC-MS/MS was recorded by Thermo Scientific/TSQ Quantum Access Max at Scientific Technical Application and Research Center at Hitit University. Absorption spectra of compounds were recorded by a PG Instruments T80+ spectrophotometer.

2.2. General synthesis of the arylhydrazone derivatives (Arilhidrazon türevlerinin genel sentezi)

Diazonium salt:
4,4'-thiodianiline (0,010 mol) or 4,4'-sulfonyldianiline (0.010 mol) was dissolved in conc. HCl (5.04 mL, 0.060 mol) and 20.00 mL of water. Then, the solution temperature was allowed down to around 0°C on an ice-salt bath and 1.38 g (0.020 mol) $NaNO_2$ solution in water was slowly dropped to the diamine solution and, continued stirring for at least 30 min. The temperature of the mixture should not exceed 0–5°C.

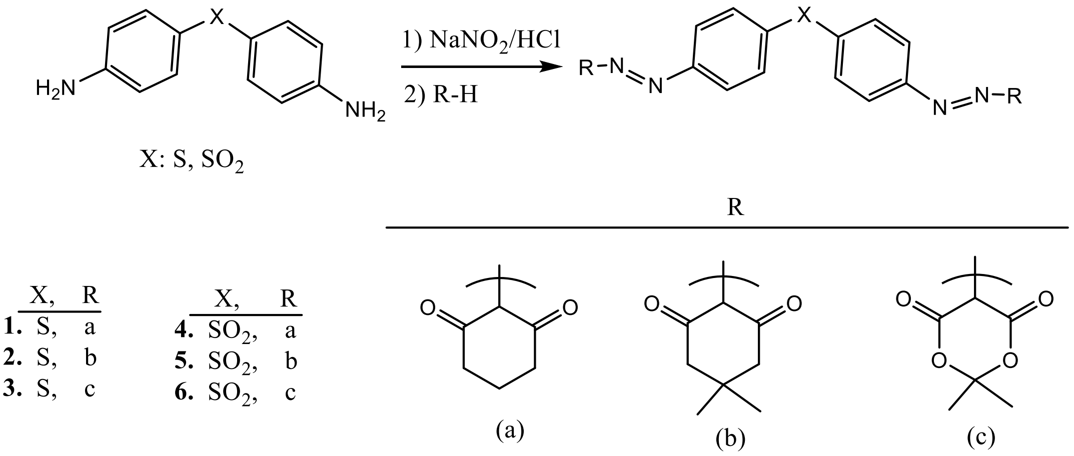

Figure 1. Synthesis of bis azo compounds (1-6) (Bis azo bileşiklerinin sentezi(1-6))

Azo coupling:

Cyclic-1,3-dicarbonyl compounds (0.010 mol) in ethanol (20 mL) were added in portions to solution of the diazonium salt at 0–5°C. This mixture maintained 3h. The solid product was precipitated with saturated sodium acetate solution under pH control. The obtained solid crude was filtered, air-dried and recrystallized using ethanol (for all compounds). The purities of the compounds were controlled with TLC (ethylacetate; n-hexane, 1:1).

*2,2'-((thiobis(4,1-phenylene))bis(hydrazin-2-yl-1-ylidene))bis(cyclohexane-1,3-dione) (**1**)*

This compound was synthesized using the 4,4'-thiodianiline and cyclohexane-1,3-dione compounds by the same procedure mentioned above for the synthesis of general procedure for the synthesis of the arylhydrazone derivatives.

Yield: 61% m.p: 233-235°C, Color: Brown; FT-IR (cm^{-1}): 3027 (Ar-H), 2952-2861 (aliph. C-H), 1690 and 1668 (2C=O), 1574 and 1496 (2N=N); ^{1}H-NMR $CDCl_3$ (ppm): 15.47 (s, 2H, N-H), 7.55 (d, 4H, J=8.7 Hz, Ar-H), 7.40 (d, 4H, J= 8.7 Hz, Ar-H), 2.75 (t, 8H, CH_2), 2.12 (m, 4H, CH_2).

*2,2'-((thiobis(4,1-phenylene))bis(hydrazin-2-yl-1-ylidene))bis(5,5-dimethylcyclohexane-1,3-dione) (**2**)*

This compound was synthesized using the 4,4'-thiodianiline and dimedone compounds by the same procedure mentioned above for the synthesis of general procedure for the synthesis of the arylhydrazone derivatives.

Yield: 52% m.p: 140-142°C, Color: Brown; FT-IR (cm^{-1}): 3055 (Ar-H), 2963-2926 (aliph. C-H), 1670 and 1616 (2C=O), 1595 and 1575 (2N=N); ^{1}H-NMR $CDCl_3$ (ppm): 15.47 (s, 2H, NH), 7.54 (d, 4H, J=8.7 Hz, Ar-H), 7.38 (d, 4H, J= 8.7 Hz, Ar-H), 2.64 (s, 4H, CH_2), 2.13 (s, 4H, CH_2), 1.16 (s, 12H, CH_3).

*2,2'-((thiobis(4,1-phenylene))bis(hydrazin-2-yl-1-ylidene))bis(2,2-dimethyl-1,3-dioxane-4,6-dione) (**3**)*

This compound was synthesized using the 4,4'-thiodianiline and 2,2-dimethyl-1,3-dioxane-4,6-dione compounds by the same procedure mentioned above for the synthesis of general procedure for the synthesis of the arylhydrazone derivatives.

Yield: 43% m.p: 178-180°C, Color: Orange; FT-IR (cm^{-1}): 3100 (Ar-H), 2996-2943 (aliph. C-H), 1743 and 1695 (2C=O), 1590 and 1516 (2N=N); ^{1}H-NMR $CDCl_3$ (ppm): 13.70 (s, 2H, NH), 7.52 (d, 4H, J= 8.7 Hz, Ar-H), 7.44 (d, 4H, J= 8.7 Hz, Ar-H), 1.84 (s, 12H, CH_3)

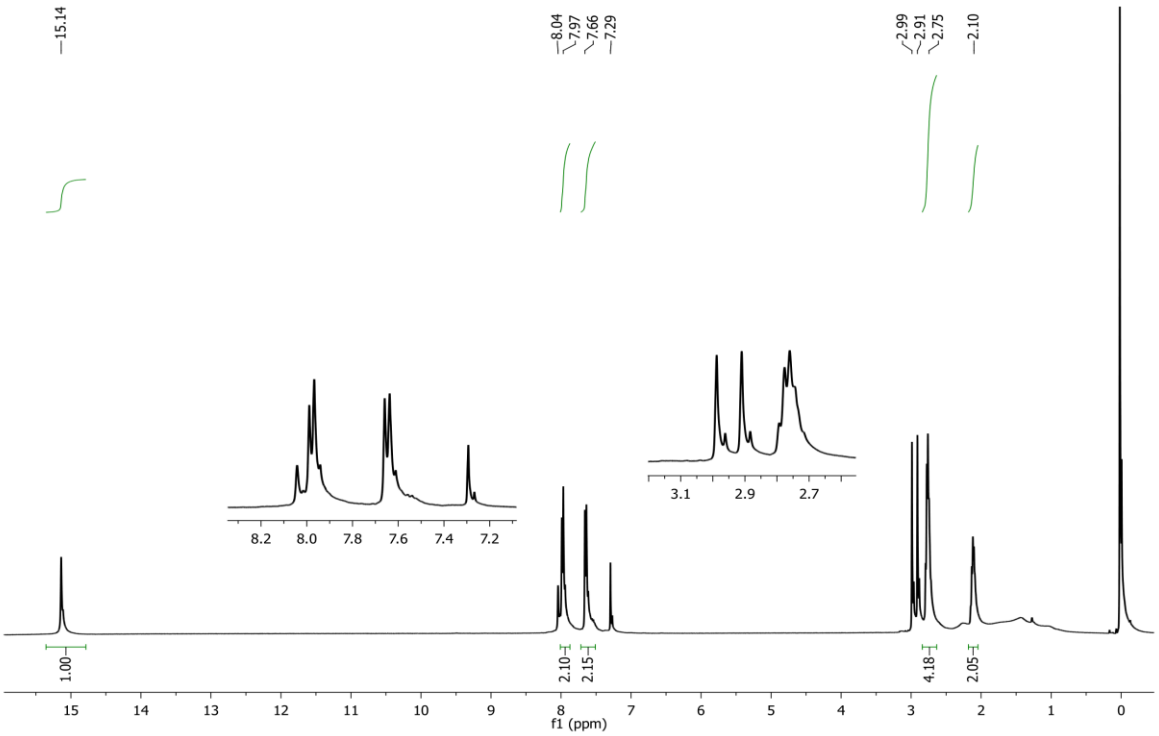

Figure 2. ^{1}H-NMR spectrum of compound 4 (Bileşik 4’ün ^{1}H-NMR spektrumu)

*2,2'-((sulfonylbis(4,1-phenylene))bis(hydrazin-2-yl-1-ylidene))bis(cyclohexane-1,3-dione) (**4**)*

This compound was synthesized using the 4,4'-sulfonyldianiline and cyclohexane-1,3-dione compounds by the same procedure mentioned above for the synthesis of general procedure for the synthesis of the arylhydrazone derivatives.

Yield: 60% m.p: 229-231°C, Color: Dark brown; FTIR (cm^{-1}): 3095 (Ar-H), 2941-2875 (aliph. C-H), 1668 and 1635 (2C=O), 1588 and 1573 (2N=N); ^1H-NMR $CDCl_3$ (ppm): 15.14 (s, 2H, NH), 7.97 (d, 4H, J= 8.7 Hz, Ar-H), 7.66 (d, 4H, J= 8.7 Hz, Ar-H), 2.75 (t, 8H, CH_2), 2.10 (m, 4H, CH_2).

*2,2'-((sulfonylbis(4,1-phenylene))bis(hydrazin-2-yl-1-ylidene))bis(5,5-dimethylcyclohexane-1,3-dione) (**5**)*

This compound was synthesized using the 4,4'-sulfonyldianiline and dimedone compounds by the same procedure mentioned above for the synthesis of general procedure for the synthesis of the arylhydrazone derivatives.

Yield: 79% m.p: 258-260°C, Color: Yellow; FT-IR (cm^{-1}): 3039 (Ar-H), 2955-2930 (aliph. C-H), 1683 and 1634 (2C=O), 1594 and 1580 (2N=N); ^1H-NMR $CDCl_3$ (ppm): 15.13 (s, 2H, NH), 7.99 (d, 4H, J= 8.6 Hz, Ar-H), 7.66 (d, 4H, J= 8.6 Hz, Ar-H), 2.66 (s, 4H, CH_2), 2.16 (s, 4H, CH_2), 1.16 (s, 12H, CH_3)

*2,2'-((sulfonylbis(4,1-phenylene))bis(hydrazin-2-yl-1-ylidene))bis(2,2-dimethyl-1,3-dioxane-4,6-dione) (**6**)*

This compound was synthesized using the 4,4'-sulfonyldianiline and 2,2-dimethyl-1,3-dioxane-4,6-dione compounds by the same procedure mentioned above for the synthesis of general procedure for the synthesis of the arylhydrazone derivatives.

Yield: 81% m.p: 293-295°C, Color: Brown; FT-IR (cm^{-1}): 3102 (Ar-H), 2996-2939 (aliph. C-H), 1743 and 1696 (2C=O), 1590 and 1516 (2N=N); ^1H-NMR $CDCl_3$ (ppm): 13.56 (s, 2H, NH), 8.03 (d, 4H, J= 8.8 Hz, Ar-H), 7.66 (d, 4H, J= 8.8 Hz, Ar-H), 1.84 (s, 12H, CH_3).

3. RESULTS (BULGULAR)

3.1. FT-IR and ^{1}H-NMR Studies (FT-IR ve ^{1}H-NMR çalışmaları)

Three tautomeric forms that bis azo-dioxo (T1), bis hydrazo-dioxo (T2) and bis azo-enol-oxo (T3) were estimated for bis azo dyes regarding present FT-IR and ^1H-NMR data. The structures of **1-6** are confirmed by the presence of corresponding signals of the FT-IR and ^1H-NMR protons spectra. The estimated tautomeric forms are shown in Figure 3 on the bis azo compound **1**.

In the FT-IR spectrum of bis azo compounds 1-6, it was observed characteristic absorption bands; for aromatic proton peaks around 3027, 3055, 3100, 3095, 3039 and 3102 cm^{-1} respectively, for aliphatic C-H peaks between 2996–2861 cm^{-1}, for C=O peaks between 1743–1616 cm^{-1}, and for N=N peaks between 1595–1496 cm^{-1}. It is predicted regarding FT-IR analysis data that the synthesized bis azo dyes are bis azo-dioxo (T1) tautomeric form in solid [39].

3.2. UV-Vis Study

The UV-Vis spectra of the bis azo dyes were recorded in 4 different solvents; chloroform, DMF, acetic acid, and methanol (Figure 4). Solvents in different polarities were preferred in our study. In addition, the acidic or basic medium impacts on the absorption spectra of bis azo dyes were investigated [38]. For this purpose, 2–3 mL of HCl (0.1 M) or KOH (0.1 M) solution was added to the bis azo-methanol solution and scanned again. All measurements were recorded at room temperature (±25°C). The data obtained are listed in Table 1.

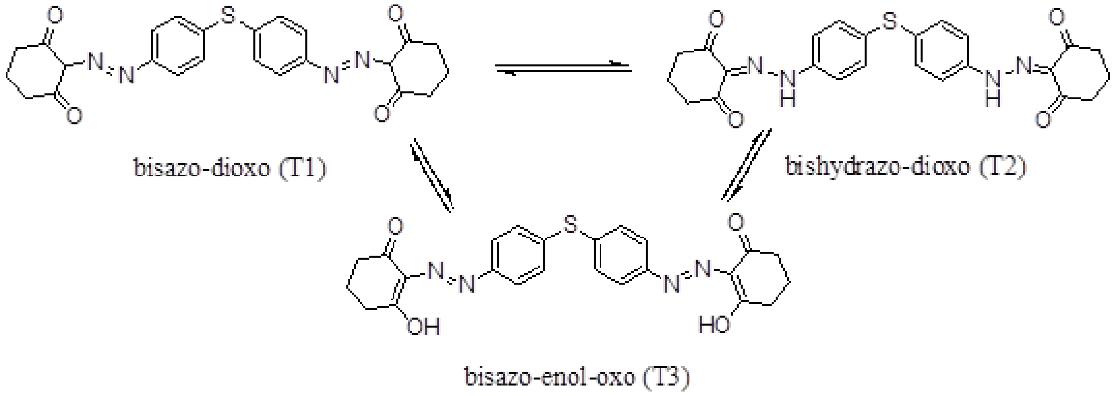

Figure 3. Tautomeric forms of compound **1**. (Bileşik 1'in tautomerik formları)

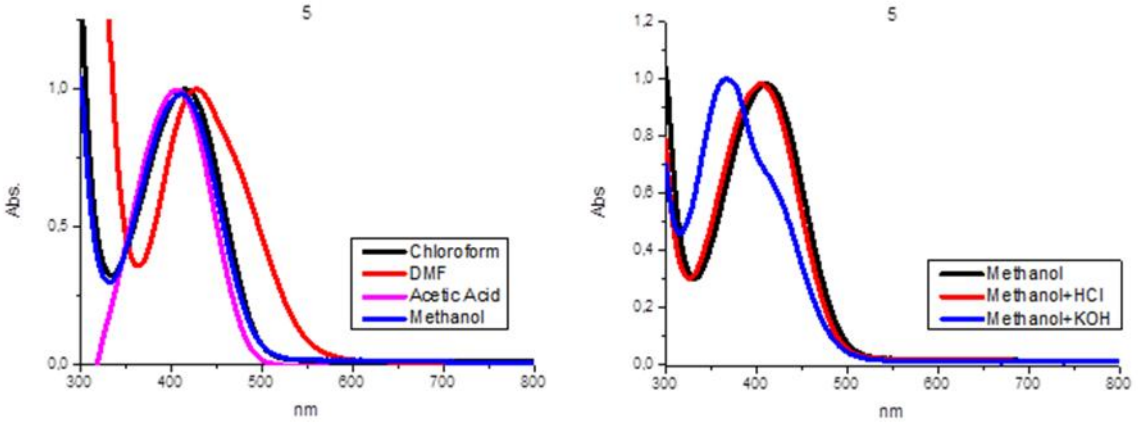

Figure 4. Absorption spectra of **5** in solution of different solvents (Farklı çözücülerin çözeltisinde **5**'in absorpsiyon spektrumları)

3.3. LC MS/MS Study

While the mass spectra were taken, the samples were dissolved in methanol and then filtered through the 0.45µm syringe filter. The structures of **1-6** bis azo dyes were proposed considering these LC-MS/MS data and the molecular weight information. The molecular ion cluster was determined at m/z 462.03 for **1**, 517.00 for **2**, 525.10 for **3**, 494.89 for **4** (Figure.5), 550.22 for **5**, 556.88 for compound **6** respectively.

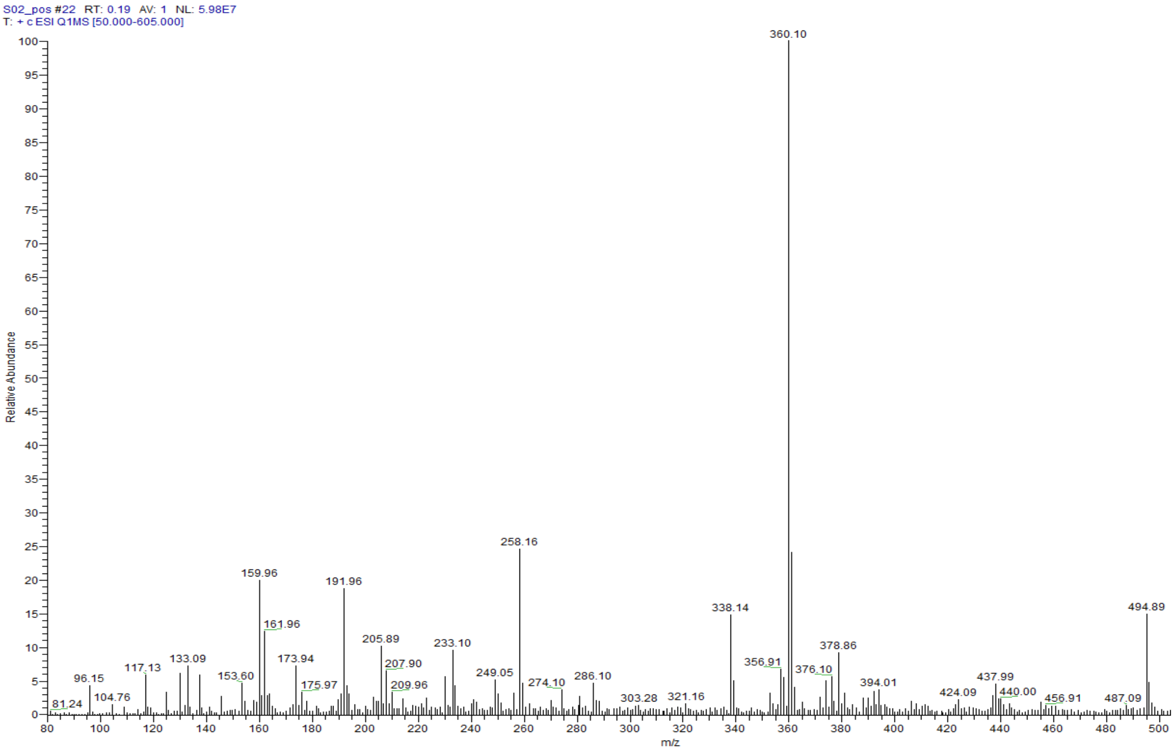

Figure 5. LC MS/MS spectrum of compound **4** (Bileşik **4**'ün LC MS/MS spektrumu)

4. CONCLUSIONS (SONUÇLAR)

In the ^{1}H-NMR Spectrum, we can say that our compounds are in bishydrazo-dioxo form because NH protons come out in a very low field between 15.56–13.70 ppm. In the literature, the reaction of cyclic-1,3-dicarbonyl compounds with the aryldiazonium compounds gave the arylhydrazo derivatives and these compounds are in the arylhydrazo form via the intramolecular N-H–O=C-hydrogen bonding [36, 37]. Although bishydrazo-dioxo form (T2) appears in solution, in the FT-IR spectra, the solvent-free medium, has not been observed either. These results are in agreement with the literature [40, 41].

Table 1. The maxima absorption points of bis azo dyes in different solvents (Bis azo boyalarının farklı solventlerdeki maksimum absorpsiyon noktaları)

λ_{max} (nm)						
	Chloroform	**DMF**	**Acetic acid**	**Methanol**	**Methanol+HCl**	**Methanol+KOH**
1	440	450	428	442	435	379, 460^{s}
2	392	404	386	389	385	397, 486^{s}
3	440	452	430	433	421	376, 455^{s}
4	388	409, 500^{s}	381	385	379	398, 450^{s}
5	416	428	406	411	405	367, 419^{s}
6	390	401	382	392	386	403, 634^{s}

s: shoulder

Solvent polarity is one of the factors that cause changes in absorption values in UV-Vis spectra. A hypsochromic shift up to 6–10 nm was observed in acetic acid and a bathochromic shift (≥10 nm) in DMF compared to chloroform in all synthesized diazo dyes, besides no clear change in methanol. It has been observed generally that bis azo dyes containing the sulfonyl group have a more low wavelength as against the sulfo group in all solutions. According to the absorption data, it can be said that a single maximum absorption peak was observed in all solvents. This situation suggested that the bis azo dye solutions consisted of a single tautomeric form. According to our explanation based on the NMR data before, the compounds are thought to be mostly in the bis hydrazo-dioxo (T2) tautomeric form in the solution medium. Also, a shoulder peak at 500 nm is observed in the spectrum of compound 4 recorded in DMF. This situation suggests a mixture of the two tautomeric forms in DMF.

The acidic or basic medium impacts on the absorption spectra of dye solutions were investigated by adding HCl or KOH to the methanol solution. For all dye solutions, it has been observed hypsochromic shift (in values ranging from 4 to 8 nm) in absorption values in an acidic medium. Only a single absorption peak is observed in the acidic media spectra, suggesting that it is in a single tautomeric form. In basic medium, a bathochromic shift can be mentioned for all compounds, but long wavelength shouldering (>400 nm) was also observed in all recorded spectra. This situation shows that two different tautomeric forms coexist in the basic environment of dye solutions.

DECLARATION OF ETHICAL STANDARDS (ETİK STANDARTLARIN BEYANI)

The author of this article declares that the materials and methods they use in their work do not require ethical committee approval and/or legal-specific permission.

Bu makalenin yazarı çalışmalarında kullandıkları materyal ve yöntemlerin etik kurul izni ve/veya yasal-özel bir izin gerektirmediğini beyan ederler.

AUTHORS' CONTRIBUTIONS (YAZARLARIN KATKILARI)

Gülnihal ERTEN**:** She conducted the experiments, analyzed the results and performed the writing process.

Deneyleri yapmış, sonuçlarını analiz etmiş ve makalenin yazım işlemini gerçekleştirmiştir.

Naki ÇOLAK**:** He analyzed the results and performed the writing process.

Deney sonuçlarını analiz etmiş ve makalenin yazım işlemini gerçekleştirmiştir.

CONFLICT OF INTEREST (ÇIKAR ÇATIŞMASI)

There is no conflict of interest in this study.

Bu çalışmada herhangi bir çıkar çatışması yoktur.

REFERENCES (KAYNAKLAR)

[1] Albertin G, Antoniutti S, Boato M. Diazo Complexes of Osmium: Preparation of Binuclear Derivatives with Bis (Aryldiazene) and Bis (Aryldiazenido) Bridging Ligands. Inorg. Chim. Acta, 357 (2004) 1119–1133.

[2] Raghu AV, Gadaginamath GS, Mathew NT, Halligudi SB, Aminabhavi TM,.Synthesis and Characterization of Novel Polyurethanes Based on 4,4-[1,4-Phenylenedidiazene-2,1-Diyl]Bis(2-Carboxyphenol) and 4,4- [1,4-Phenylenedi-Diazene-2,1-Diyl]Bis(2-Chlorophenol) Hard Segments. React. Func. Polym. 67 (2007) 503–514.

[3] Shchur IV, Khudina OG, Burgart YV, Saloutin VI, Grishina MA, Potemkin VA. Synthesis, Structure, and Complexing Ability of Fluoroalkylcontaining 2,2-(Biphenyl-4,4-Diyldihydrazono)Bis(1,3-Dicarbonyl) Compounds. Russ. J. Org. Chem. 43 (2007) 1781–1787.

[4] Weaver MA, Shuttleworth L. Heterocyclic diazo components. Dye Pigm. 3 (1982) 81-121.

[5] Urus S, Ozdemir M, Ceyhan G, Tumer M. Chemically Modified Silica-Gel With an Azo-Schiff Ligand and Its Metal Complexes with Cu(II), Co(II), Ni(II) and Mn(II): Applications as Catalysts on the Oxidation of Cyclohexane Under Microwave Power. Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 42 (2012) 382–391.

[6] Kitaev YP, Buzykin BI, (1974). Gidrazony [Hydrazones], Nauka, Moscow, 416 pp. (in Russian).

[7] Kost AN, Grandberg II. Progress in Pyrazole Chemistry. Adv. Heterocycl. Chem., 6 (1966) 347-429.

[8] Jeong MJ, Park JH, Lee C, Chang JY. Discotic Liquid Crystalline Hydrazone Compounds: Synthesis and Mesomorphic Properties. Org. Lett. 8 (2006) 2221–2224.

[9] Chen Z, Wu Y, Gu D, Gan F. Nickel (II) and Copper (II) Complexes Containing 2-(2-(5-Substitued İsoxazol-3-Yl)Hydrazono)-5,5-Dimethylcyclohexane-1,3-Dione Ligands: Synthesis, Spectral and Thermal Characterizations. Dyes Pigm. 76 (2008) 624–631.

[10] Sokolnicki J, Legendziewicz J, Amirkhanov W, Ovchinnikov V, Macalik L, Hanuza J. Comparative Optical Studies of Lanthanide Complexes with Three Types of Phosphoro-Azo Derivatives of Β-Diketones. Spec. Chim. Acta A. 55 (1999) 349–367.

[11] More MS, Joshi PG, Mishra YK, Khanna PK. Metal Complexes Driven from Schiff Bases fnd Semicarbazones for Biomedical and Allied Applications: A Review. Mater. Today Chem., 14 (2019) 100195–100217.

[12] Torres MJ, Criado A, Ruiz M, Llanos AC, Palomares JC, Aznar J. Improved Real-Time PCR for Rapid Detection of Rifampin and Isoniazid Resistance in Mycobacterium Tuberculosis Clinical Isolates. Diag. Micr. Infects Disease., 45 (2003) 207-212.

[13] Tian NZ, Zhou Y, Sun SG, Ding Y, Zhong LW. Synthesis of Tetrahexahedral Platinum Nanocrystals with High-İndex Facets and High Electro-Oxidation Activity. Sci. Mag., 316 (2007) 732-735.

[14] Raja A, Rajendiran V, Mahesweri PU, Balamuugan R, Kilner CA, Halcrow MA. Copper (II) Complexes of Tridentate Pyridylmethylethylenediamines: Role of Ligand Steric Hindrance on DNA Binding and Cleavage. J. Inorg. Biochem., 99 (2005) 1717-1732.

[15] Abdel-Rahman LH, Abu-Dief AM, Ismail M, Ismael NM. Synthesis, Characterization, And Biological Activity of New Mixed Ligand Transition Metal Complexes of Glutamine, Glutaric, and Glutamic Acid with Nitrogen Based Ligands. Inorg. Nano-Metal Chem., 47 (2017) 467-480.

[16] Maria CSL, Marcelle LF, Marcus VNS, Monica AP, Thatyana RAV, Maria G, Henriques MO. Synthesis and Anti-Mycobacterial Activity of (E)-N′-(mono substituted-benzylidene)isonicotino hydrazide Derivatives Eur. J. Med. Chem., 43 (2008) 1344-1347.

[17] Samir AC, Edson FS, Marcus VN, Maria CSL, Felipe RV. Synthesis and Antimycobacterial Evaluation of New Trans-Cinnamic Acid Hydrazide Derivatives. Bio. Org Med. Chem Lett., 18 (2008) 538-541.

[18] Manjunatha B, Bodke YD, Nagaraja O, Nagaraju G, Sridhar MA. Coumarin-Benzothiazole Based Azo Dyes: Synthesis, Characterization, Computational, Photophysical and Biological Studies. J. Mol. Struct. 1246 (2021) 131170–131185.

[19] Weldegebrieal GK. Synthesis Method, Antibacterial and Photocatalytic Activity of Zno Nanoparticles for Azo Dyes in Wastewater Treatment: A Review. Inorg. Chem. Commun. 120 (2020) 108140–108211.

[20] Gaffer HE. Antimicriobial Sulphonamide Azo Dyes, Color. Technol., 135 (2019) 484–500.

[21] Kornıs G, Katritzky AR. (ed. 1984) l,3,4-Thiadiazoles in Comprehensive Heterocyclic Chemistry, Pergamon Press, Vol. 6, Part 4B, 545-578.

[22] Allard N, Beaupre S, Aich BR, Najari A, Tao Y, Leclerc M. Synthesis and characterization of new poly (thieno[3,4-d]thiazole) derivatives for photovoltaic applications. Macromolecules, 44 (2011) 7184–7187.

[23] Zonouzi A, Rezaei MH, Mirzazadeh R, Arjomand MR. Solvent-free Synthesis of

Halogenated Furo[2,3-d] pyrimidines and Their Cytotoxic Activity on the T47D Breast Cancer Cell Line. Organic Preparations and Procedures International. 52 (2020) 374-380.

[24] Zaky RR, Yousef TA. Spectral, Magnetic, Thermal, Molecular Modelling, ESR Studies and Antimicrobial Activity of (E)-3-(2-(2-Hydroxybenzylidene) Hydrazinyl)-3-Oxo-N(Thiazole-2-Yl)Propanamide Complexes. J. Mol. Struct. 1002 (2011) 76-85.

[25] Santini C, Pellei M, Gandin V, Porchia M, Tisato F, Marzano C. Advances in Copper Complexes as Anticancer Agents Chem. Rev., 114 (2014) 815-862.

[26] Lu Y, Li CM, Wang Z, Ross CR, Chen J, Dalton JT, Li W, Miller DD. Discovery of 4-Substituted Methoxybenzoyl-Aryl-Thiazole as Novel Anticancer Agents: Synthesis, Biological Evaluation, and Structure-Activity Relationships. J. Med. Chem., 52 (2009) 1701-1711.

[27] Lombardo LJ, Lee FY, Chen P, Norris D, Barrish JC, Behnia K, Castaneda S, Cornelius LAM, Das J, Doweyko AM, Fairchild C, Hunt JT, Inigo I, Johnston K, Kamath A, Kan D, Klei H, Marathe P, Pang S, Peterson R, Pitt S, Schieven GL, Schmidt RJ, Tokarski J, Wen M-L, Wityak J, Borzilleri RM. Discovery of N-(2-Chloro-6-methyl- phenyl)-2-(6-(4-(2-hydroxyethyl)- piperazin-1-yl)-2-methylpyrimidin-4- ylamino)thiazole-5-carboxamide (BMS-354825), a Dual Src/Abl Kinase Inhibitor with Potent Antitumor Activity in Preclinical Assays. J. Med. Chem., 47 (2004) 6658-6661.

[28] Khan E, Gul Z, Shahzad A, Jan SM, Ullah F, Tahir MN. Coordination Compounds of 4,5,6,7-Tetrahydro-1H-İndazole with Cu(II), Co(II) and Ag(I): Structural, Antimicrobial, Antioxidant and Enzyme Inhibition Studies, J. Coord. Chem., 70 (2017) 4054-4069.

[29] Nagasundaram N, Govindhan C, Sumitha S, Sedhu N, Raguvaran K, Santhosh S, Lalitha A. Synthesis, Characterization and Biological Evaluation of Novel Azo Fused 2,3-Dihydro-1H-Perimidine Derivatives: In Vitro Antibacterial, Antibiofilm, Anti-Quorum Sensing, DFT, in Silico ADME and Molecular Docking Studies J. Mol. Struct. , 248 (2022) 131437–131449.

[30] Gregory P. (2002). Industrial Dyes: chemistry, Properties and Applications, Wiley- VCH, Weinheim, 543-585.

[31] Bamfield P, Hutchings MG. (2010). Chromic Phenomena: Technological Applications of Colour Chemistry, 2nd ed., RSC, Cambridge.

[32] Zollinger H. (2003). Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments, 3rd ed., Wiley-VCH, Weinheim.

[33] Çatıkkas B, Aktan E, Yalçın E. Vibrational and electronic investigations, NLO, FMO analysis on a hetarylazoindole disperse dye by density functional theory. J. Mol. Struct., 1117 (2016) 218–226.

[34] Aysha T, El-Sedik, M, Megied SAE, Ibrahim H, Youssef Hrdina YR. Synthesis, Spectral Study and Application of Solid State Fluorescent Reactive Disperse Dyes and Their Antibacterial Activity, Arab. J. Chem., 12 (2019) 225–235.

[35] Dopanay K, Keleştemur U, Balcıoğlu S, Ateş B, Altundaş A. Synthesis, Reaction, and Evaluation of The Anticancer Activity of 6,7,8,9,-Tetrahydro-5h-Cyclohepta [4,5] Selenopheno [2,3-D] Pyrimidine Derivatives. Tur J. Chem., 40 (2016) 631-640.

[36] Drew MGB. Phenylhydrazone Derivatives of Dimedone: Hydrogen Bonding, Spectral (I3C and H Nuclear Magnetic Resonance) and Conformational Considerations. Crystal and Molecular Structures Of 5,5-Dimethylcyclohexane-1, 2,3-Trione 2-(4-Methylphenylhydrazone) (1) and 5, 5-Dimethylcyclohexane-1,2,3-Trione 2-(4-Nitrophenylhydrazone) (2), J Chem Soc. Perkin Trans II, (1982) 1297–1303.

[37] Mohareb RM, Al Farouk FO, Wardakhan WW. Uses of Dimedone for the Synthesis of New Heterocyclic Derivatives with Anti-Tumor, C-Met, Tyrosine, and Pim-1 Kinases İnhibitions. Medicinal Chemistry Research, 27 (2018) 1984-2003.

[38] Silverstein RM, Bassler GC. Spectrometric identification of organic compounds. J Chem Educ. 39 (1962) 546.

[39] Karcı F, Karcı F., Synthesis and Tautomeric Structures of Some Novel Thiophene-Based Bis-Heterocyclic Monoazo Dyes, J Mol Struct., 1024 (2012) 117–122.

[40] Çiçen G, Karabacak Atay Ç, Tilki T. Disazo Dyes Containing Pyrazole and Benzothiazole Moieties: Synthesis, Characterization, Absorption Characteristics and Tautomeric Structures, Res Chem Intermed., 43 (2017), 6803-6816.

[41] Omar AZ, El-Rahman MA, El-Sadany SK, Hamed EA, El-Atawy MA. Synthesis of Novel Bisazo Disperse Dyes: Spectroscopic Characterization, DFT Study and Dyeing of Polyester, Dyes Pigm., 196 (2021), 109831.