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Novel Heterocyclic Azo Compounds: Synthesis, Characterization and DFT Calculations

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Abstract: Today, it is of great importance to synthesize new azo compounds as well as to conduct research in different areas of use. More than one usage area is increasing day by day in high-tech products (laser printing materials, printer toners, liquid crystals, etc.) as well as in many sectors such as paper, food, cosmetics, textile and leather. In this study, considering these advantages, the compounds of 3-amino-1H-pyrazol-5-ol, 1H-1,2,4-triazol-3-amine and 3-amino-5-hydroxy-1-phenyl pyrazole were used as starting materials. As a result of azo coupling of diazonium salts with resorcinol and 3,5-dihydroxy benzoic acid, new azo compounds were synthesized, their structures were characterized by spectroscopic methods such as FT-IR and ^{1}H-NMR, and different solvent effects on visible absorption spectra were investigated. Molecular geometry and vibration frequency calculations of synthesized compounds were made with Density Functional Theory (DFT) using 6-311G (d,p) basis set at the B3LYP level. Additional, electronic properties and HOMO-LUMO orbital calculations were carried out with time dependent DFT (TD-DFT) approach. As a result of this study, it has been observed that azo compounds containing heterocyclic amine groups have bathochromic effects and bright colors. It is anticipated that this study will make important contributions to the literature and the dyestuff industry and will form a basis for potential applications.

***Keywords**:* Azo compounds, Heterocyclic, Density Functional Theory

Yeni Heterosiklik Azo Bileşikler: Sentez, Karakterizasyon ve DFT Hesaplamaları

Özet: Günümüzde yeni azo bileşikleri sentezlemek ile birlikte farklı kullanım alanlarında da araştırma yapmak büyük önem taşımaktadır. Kâğıt, gıda, kozmetik, tekstil ve deri gibi birçok sektörde kullanım alanları olduğu gibi yüksek teknoloji ürünlerinde de (lazer baskı materyelleri, yazıcı tonerleri, sıvı kristaller vb.) birden fazla kullanım alanı her geçen gün giderek artmaktadır. Bu çalışmada, bu avantajlar göz önünde bulundurarak, başlangıç maddeleri olarak 3-amino-1H-pirazol-5-ol, 1H-1,2,4-triazol-3-amin ve 3-amino-5-hidroksi-1-fenil pirazol bileşiklerinin diazonyum tuzlarının resorsinol ve 3,5-dihidroksi benzoik asitle azo kenetlenmesi sonucu yeni azo bileşikleri sentezlenerek, yapıları FT-IR, ^{1}H-NMR gibi spektroskopik yöntemlerle karakterize edilmiş ve görünür bölge absorpsiyon spektrumları üzerine farklı çözücü etkisi araştırılmıştır. Sentezlenen moleküllerin moleküler geometrisi hesaplamaları, 6-311G (d,p) temel setinde B3LYP seviyesinde Yoğunluk Fonksiyonel Teorisi (DFT) ile yapılmıştır. Ayrıca HOMO-LUMO orbital hesaplamaları zamana bağlı DFT (TD-DFT) yaklaşımı ile gerçekleştirilmiştir. Yapılmış olan bu çalışma sonucunda heterosiklik amin grubu içeren azo bileşiklerinin batokromik etkiye ve parlak renklere sahip olduğu gözlemlenmiştir. Bu

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çalışmanın literatüre ve boyarmadde endüstrisine önemli katkılar sağlayacağı ve potansiyel uygulamalara temel oluşturacağı öngörülmektedir.

Anahtar kelimeler: Azo bileşikleri, Heterosiklik, Yoğunluk Fonksiyonel Teorisi

1. Introduction

Azo compunds are colored organic substances which are synthesized by diazotization of primary aromatic amines and then combination with heterocyclic structure such as pyrazole and thiazole under appropriate experimental conditions [1]. The design and synthesis of different azo derivatives with heterocyclic moiety have been extensively studied for their use in numerous fields such as optics, electrochemistry and biology for the improvement of energy storage appliances, sensors and drugs [2–6].

Pyrazoles, thiazoles and their derivatives continue to attract attention by reason of their versatile and disparate applications in numerous fields. While these types of compounds are used in the synthesis of all kinds of dyes, they are mostly used in the preparation of azo dyes. Due to the nitrogen and sulfur atom located in the central core, they tend to exhibit bathochromic shift ranging from red to green and bright, deep color strength [7–10].

One of the crucial and functional methods used to explain the chemical and electronic structure of the molecule is Density Functional Theory (DFT). These method, which have been used frequently in recent years, is similar to other quantum mechanical methods in many ways. The DFT method is more attractive than other methods because it includes electron correlation in its calculations by which more accurate and precise results can be obtained [11].

In this study, based on the above considerations the compounds of 3-amino-1H-pyrazol-5-ol, 1H-1,2,4-triazol-3-amine and 3-amino-5-hydroxy-1-phenyl pyrazole were used as starting materials. For the reason that the azo coupling of diazonium salts with resorcinol and 3,5-dihydroxy benzoic acid, new azo compounds were synthesized, their structures were analyzed by spectroscopic methods such as FT-IR and ^{1}H-NMR, and different solvent effects on visible absorption spectra were investigated. Molecular geometry calculations of obtained compounds were made with Density Functional Theory (DFT) using 6-311G (d,p) basis set and B3LYP level. More than that, HOMO-LUMO orbital calculations were performed with time dependent DFT (TD-DFT) technique.

2. Material and Method

2.1 Physical measurements

Chemicals used for the synthesis of azo compounds: 3-amino-1H-pyrazol-5-ol, 1H-1,2,4-triazol-3-amine, 3-amino-5-hydroxy-1-phenyl pyrazole, 3,5-dihydroxy benzoic acid, resorcinol, sodium nitrite, sodium acetate, hydrochloric acid and these chemicals were used in synthesis without being purified because of their sufficient purity. These chemicals are provided from Aldrich and Merck. FT-IR spectra was recorded by preparing KBr discs with Shimadzu IR Prestige-21 Fourier Transform Infrared spectrophotometer. Also, UV-Vis spectra was recorded with Shimadzu UV-1601 and ^{1}H-NMR spectra was obtained with Bruker-SpectrospinAvance DPX 400 Ultra-Shield spectrometer in dimethylsulfoxide (DMSO-d_6) using tetramethylsilane (TMS) as the internal reference.

2.2 Chemical synthesis

All azo compounds were synthesized as stated in general procedure 2.2.1. The general synthesis scheme of all synthesized compounds is given in Figure 1.

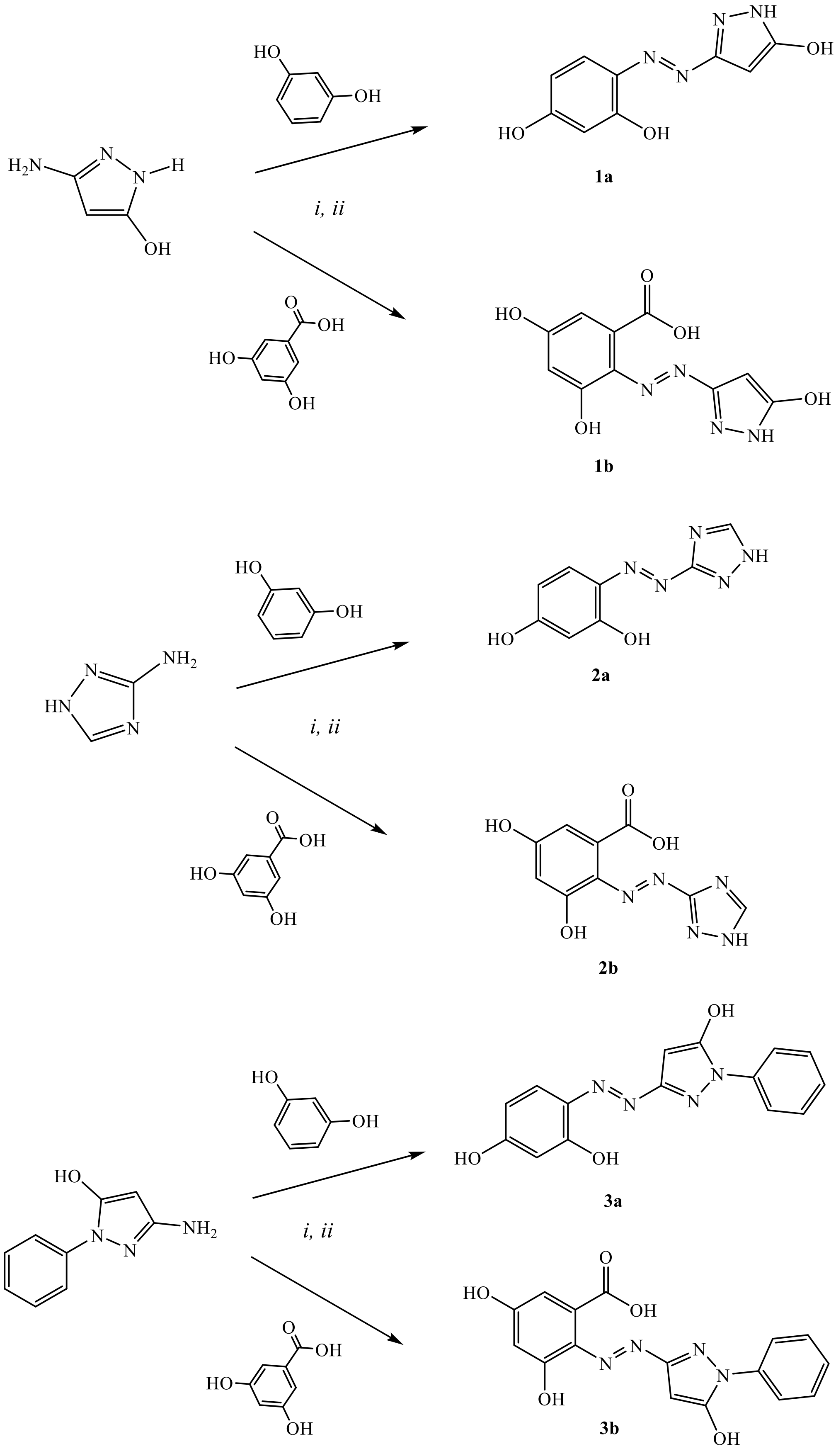

Figure 1. General synthesis scheme for the preparation of heterocyclic azo compounds. Reagents&conditions : (*i*) $NaNO_2$, HCl, H_2O, 0-(-5) ^oC, (*ii*) $CH_3COONa{\cdot}3H_2O$, H_2O, EtOH, 0-(-5) ^oC.

2.2.1 Synthesis of 4-((5-hydroxy-1H-pyrazol-3-yl) diazenyl) benzene-1,3-diol (1a)

Distilled water and HCl, 5 mL each, were added to 3-amino-1H-pyrazol-5-ol (0.01 mol; 0.99 g) and allowed to stir in an ice-salt bath. Sodium nitrite solution was prepared by adding 5 mL of distilled water to 0.7 g (0.01 mol) $NaNO_2$. The prepared solution was added to the other mixture drop by drop. The mixture stirred for 1 hour with continuous temperature control at -5 °C to form the diazonium salt. To prepare the coupling component, resorcinol (0.01 mol; 1.11 g) was dissolved in distilled water and ethanol in another salt-ice bath, and 2 grams (0.01 mol) sodium acetate (CH_3COONa) was added and mixed in an ultrasonic homogenizer until dissolved. In this step of diazotization, the diazonium salt was slowly added to the prepared solution as the coupling component. It was stirred in an ice-salt bath at -5 °C for 4 hours. The product was precipitated by saturating the reaction mixture with pure water. It was left overnight at 4 °C, filtered, washed with cold water and dried under vacuum. Yield: 44.5%. Color: dark red, **Mp**: 253-255 °C. **FT-IR** (KBr): ν_{max}= (-OH): 3178 cm^{-1}; (C=C): 1610 cm^{-1} ; (N=N): 1570 cm^{-1}. **^{1}H-NMR** (DMSO-d_6): δ (ppm) = 11.46 (s; 1H, NH), 10.87 (s; 1H, OH), 10.44 (s; 2H, OH), 7.65 (d; J ≈ 9.5 Hz, 1H, Ar-H), 6.53 (s; 1H, Ar-H), 6.45 (s; 1H, Ar-H), 6.18 (d; J ≈ 9.4 Hz, 1H, Ar-H).

2.2.2 Synthesis of 3,5-dihydroxy-2-((5-hydroxy-1H-pyrazol-3-yl)diazenyl) benzoic acid (1b)

The starting material 3-amino-1H-pyrazol-5-ol (0.99 g; 0.01 mol) was coupled with 3,5-dihydroxy benzoic acid (1.54 g; 0.01 mol) as stated in the general procedure in section 2.2.1. and the compound (**1b**) was synthesized. Yield: 45%, Color: dark red, **Mp**: 214-216 °C. **FT-IR** (KBr): ν_{max}= (-OH): 3176 cm^{-1}; (C=O): 1705 cm^{-1} ; (N=N): 1530 cm^{-1}. **^{1}H-NMR** (DMSO-d_6): δ (ppm) = 15.09 (s; 1H, OH), 13.58 (s; 1H, NH), 11.50 (s; 1H, OH), 10.97 (s; 1H, OH), 10.47 (s; 1H, OH), 6.80 (s; 2H, Ar-H), 6.43 (s; 1H, Ar-H).

2.2.3 Synthesis of 4-((1H-1,2,4-triazol-3-yl)diazenyl)benzene-1,3-diol (2a) [12,13]

The starting material 1H-1,2,4-triazole-3-amine (0.84 g; 0.01 mol) was coupled with 3,5-dihydroxy resorcinol (1.1 g; 0.01 mol) as stated in the general procedure in section 2.2.1. and the compound (**2a**) was synthesized. Yield: 44%, Color: orange, **Mp**: 183-185 °C. **FT-IR** (KBr): ν_{max}= (-OH): 3174 cm^{-1}; (C=C): 1613 cm^{-1} ; (N=N): 1472 cm^{-1}. **^{1}H-NMR** (DMSO-d_6): δ (ppm) = 11.60 (s; 1H, NH), 10.88 (s; 2H, OH), 8.53 (s; 1H, Ar-H), 7.69 (d, J ≈ 8.6 Hz, 1H, Ar-H), 6.52 (d, J ≈ 8.5 Hz, 1H, Ar-H), 6.41 (s; 1H, Ar-H).

2.2.4 Synthesis of 2-((1H-1,2,4-triazol-3-yl)diazenyl)-3,5-dihydroxy benzoic acid (2b)

The starting material 1H-1,2,4-triazole-3-amine (0.84 g; 0.01 mol) was coupled with 3,5-dihydroxy benzoic acid (1.54 g; 0.01 mol) as stated in the general procedure in section 2.2.1. and the compound (**2b**) was synthesized. Yield: 70%, Color: dark red, **Mp**: 179-181 °C. **FT-IR** (KBr): ν_{max}= (-OH): 3081 cm^{-1}; (C=O): 1717 cm^{-1} ; (N=N): 1456 cm^{-1}. **^{1}H-NMR** (DMSO-d_6): δ (ppm) = 12.65 (s; 1H, NH), 11.34 (s; 2H, OH), 8.65 (s; 1H, Ar-H), 6.68 (d, J ≈ 2.3 Hz, 1H, Ar-H), 6.51 (d, J ≈ 2.5 Hz, 1H, Ar-H).

2.2.5 Synthesis of 4-((5-hydroxy-1-phenyl-1H-pyrazol-3-yl)diazenyl)benzene-1,3-diol (3a)

The starting material 3-amino-5-hydroxy-1-phenyl pyrazole (1.75 g; 0.01 mol) was coupled with resorcinol (1.1 g; 0.01 mol) as stated in the general procedure in section 2.2.1. and the compound (**3a**) was synthesized. Yield: 53%, Color: dark red, **Mp**: 190-193 °C. **FT-IR** (KBr): ν_{max}= (-OH): 3178 cm^{-1}; (C=C): 1625 cm^{-1} ; (N=N): 1488 cm^{-1}. **^{1}H-NMR** (DMSO-d_6): δ (ppm) = 14.64 (s; 1H, OH), 14.27 (s; 1H, OH), 13.75 (s; 1H, OH), 7.98 – 7.78 (m; 5H, Ar-H), 7.25 (d; J ≈ 8.0 Hz, 1H, Ar-H), 7.20 (s; 1H, Ar-H), 7.13 (s; 1H, Ar-H), 6.19 (d, J ≈ 8.0 Hz, 1H, Ar-H).

2.2.6 Synthesis of 3,5-dihydroxy-2-((5-hydroxy-1-phenyl-1H-pyrazol-3-yl)diazenyl) benzoic acid (3b)

The starting material 3-amino-5-hydroxy-1-phenyl pyrazole (1.75 g; 0.01 mol) was coupled with 3,5-dihydroxy benzoic acid (1.54 g; 0.01 mol) as stated in the general procedure in section 2.2.1. and the compound (**3b**) was synthesized. Yield: 45%, Color: dark red, **Mp**: 185-187 °C. **FT-IR** (KBr): ν_{max}= (-OH): 3174 cm-1; (C=O): 1701 cm-1 ; (N=N): 1488 cm^{-1}. **^{1}H-NMR** (DMSO-d_6): δ (ppm) = 14.66 (s; 1H, OH), 13.74 (s; 1H, OH), 10.28 (s; 1H, OH), 8.09 – 7.71 (m; 5H, Ar-H), 7.13 (s; 1H, Ar-H), 6.81 (s; 1H, Ar-H), 6.43 (s; 1H, Ar-H).

2.3 Computational details

All visualizations and quantum chemical calculations were carried out using Avogadro 1.2.0 and Gaussian 09 programs, respectively [14-16]. Geometry optimization was done by DFT method using Becke-3-Lee-Yang-Parr (B3LYP) functional with 6-311G(d,p) basis set in gas phase [17–19]. HOMO-LUMO orbitals were calculated by TD-DFT method at the B3LYP level with same basis set.

3. Results

Heterocyclic azo compounds containing phenolic groups were synthesized and their structures were confirmed by spectroscopic methods (FT-IR and ^{1}H-NMR). Geometry optimization of the synthesized compounds were formed applying B3LYP functional with 6-311G(d,p) basis set in gas phase. Fully optimized geometry of the synthesized compounds were shown in Figure 2.

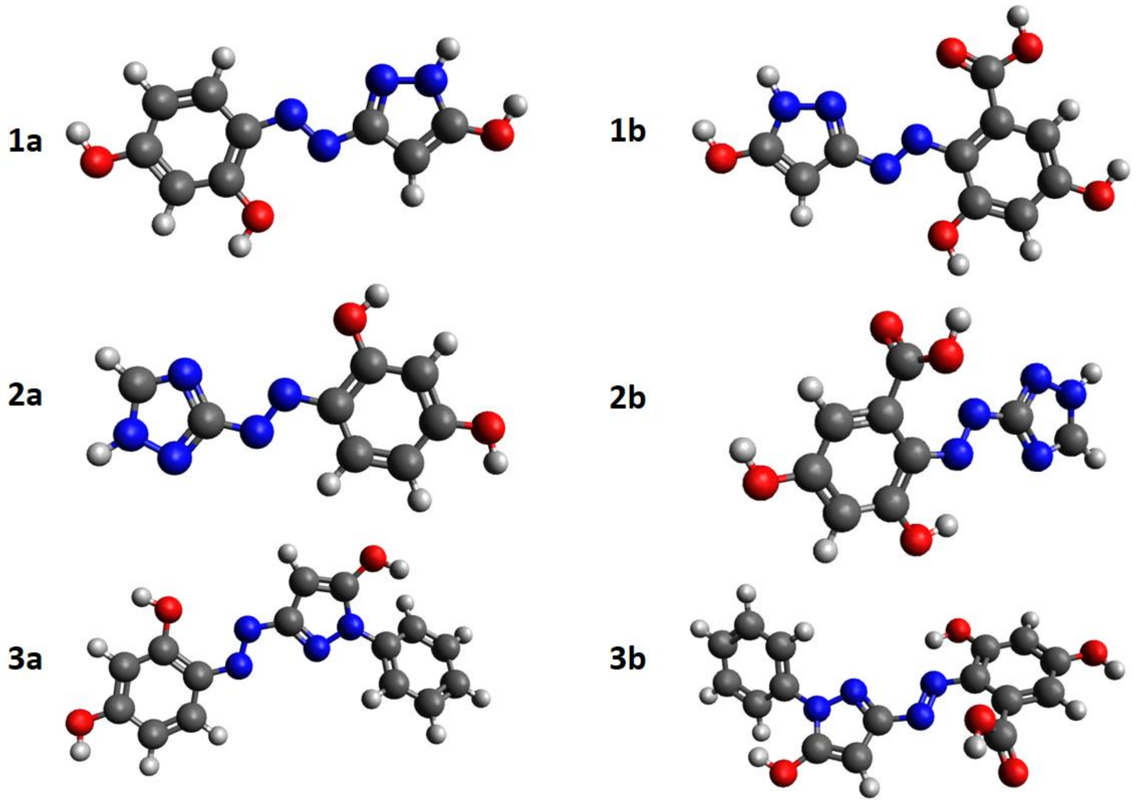

Figure 2. Calculated optimized geometry of the synthesized compounds at the B3LYP/6-311G(d,p) level.

In order to survey the solvent effect on the absorption spectra of the synthesized compounds, the visible region absorption spectra in acetic acid, DMSO, DMF and methanol and the variation of the maximum absorption wavelengths in these solvents were investigated. The bathochromic and hypsochromic shift values of the compounds were compared with each other. Maximum absorption values in the measurements performed between 300-600 nm are given in Table 1.

Table 1. Influence of different solvents on λ_{max} (nm) of **1a-b**, **2a-b** and **3a-b**

Compound	DMSO	DMF	MeOH	AcOH
1a	455	451	446	443
1b	460	456	452	453
2a	382	381	380	380
2b	378	486	384	389
3a	492	492	483	490
3b	493	488	490	485

When the visible absorption spectra of compound **1a** were examined, the λ_{max} value in DMF and DMSO showed bathochromic shift, while acetic acid and methanol showed a slightly more hypsochromic shift. It was observed that the absorption maxima of compound **1b** did not change much. However, the λ_{max} values in DMF and DMSO showed more bathochromic shift than other solvents. The spectra of compound **2a** in DMSO, DMF, acetic acid and methanol were symmetrical and a single peak absorption was detected. When the λ_{max} values of compound **2a** except DMF were examined, the absorption maximum did not change much with the solvents and showed hypsochromic shift. The λ_{max} value of compound **2b** in DMSO and methanol shows hypsochromic shift compared to other solvents. On the other hand, it differs from all other solvents and more towards bathochromic shift is observed in DMF. Unlike the others, compound **3a** and **3b** showed bathochromic shift in all solvents. The absorption spectra of the synthesized compounds in various solvents are given in Figure 3.

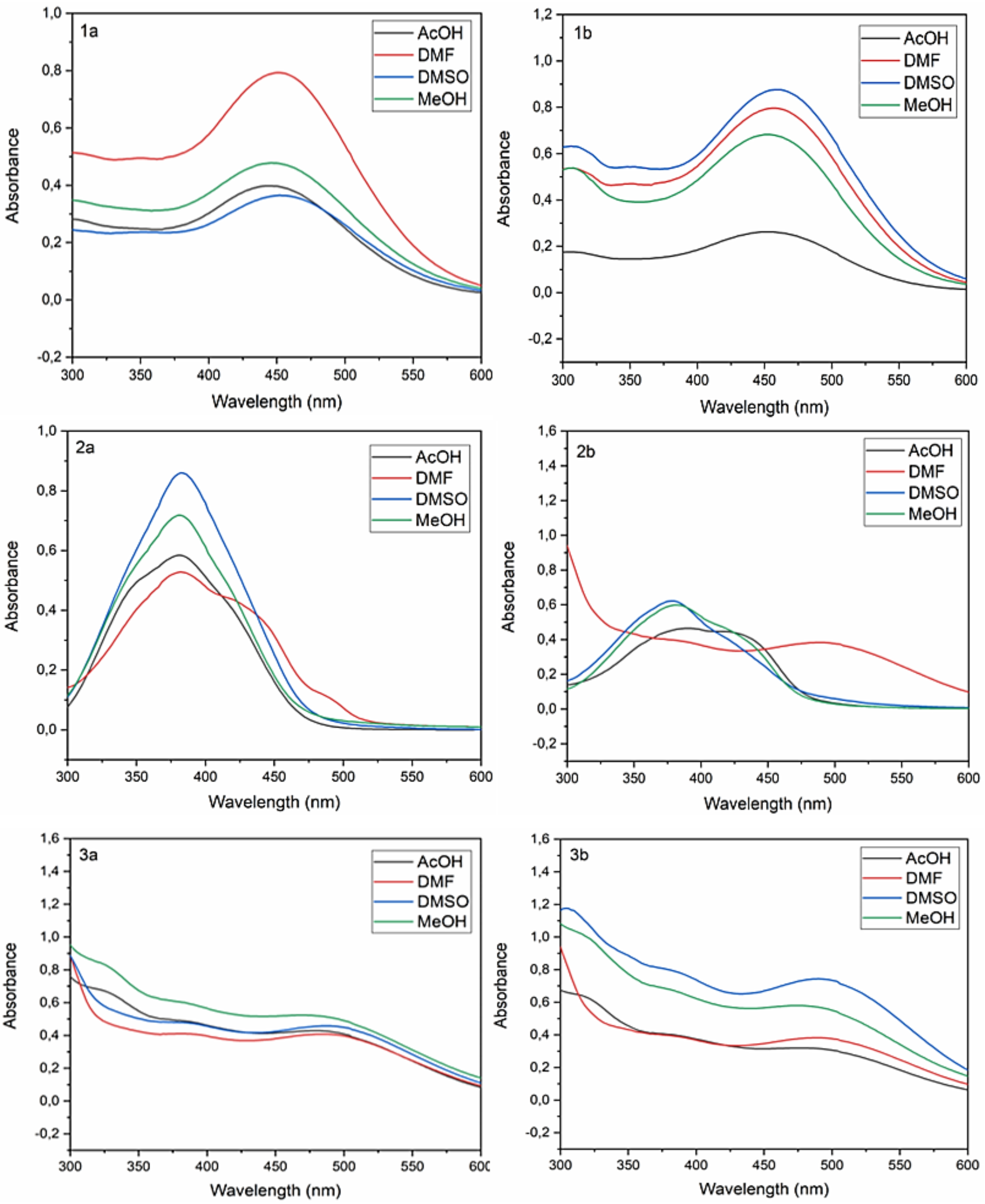

Figure 3. Absorption spectra of synthesized compounds in various solvents

Frontier orbitals called HOMO and LUMO are the essential orbitals in molecules for reactivity. HOMO is an orbital with a nucleophilic character and an electron donor, while LUMO is an electrophilic character and receives electrons. The energy gap between these frontier orbitals is one of the basic properties of molecules and gives important information about the properties of compounds such as stability and electronics. The energies of the HOMOs and LUMOs of the synthesized compounds shown in Figure 4 were calculated at the DFT / B3LYP / 6-311G (d,p) theory level.

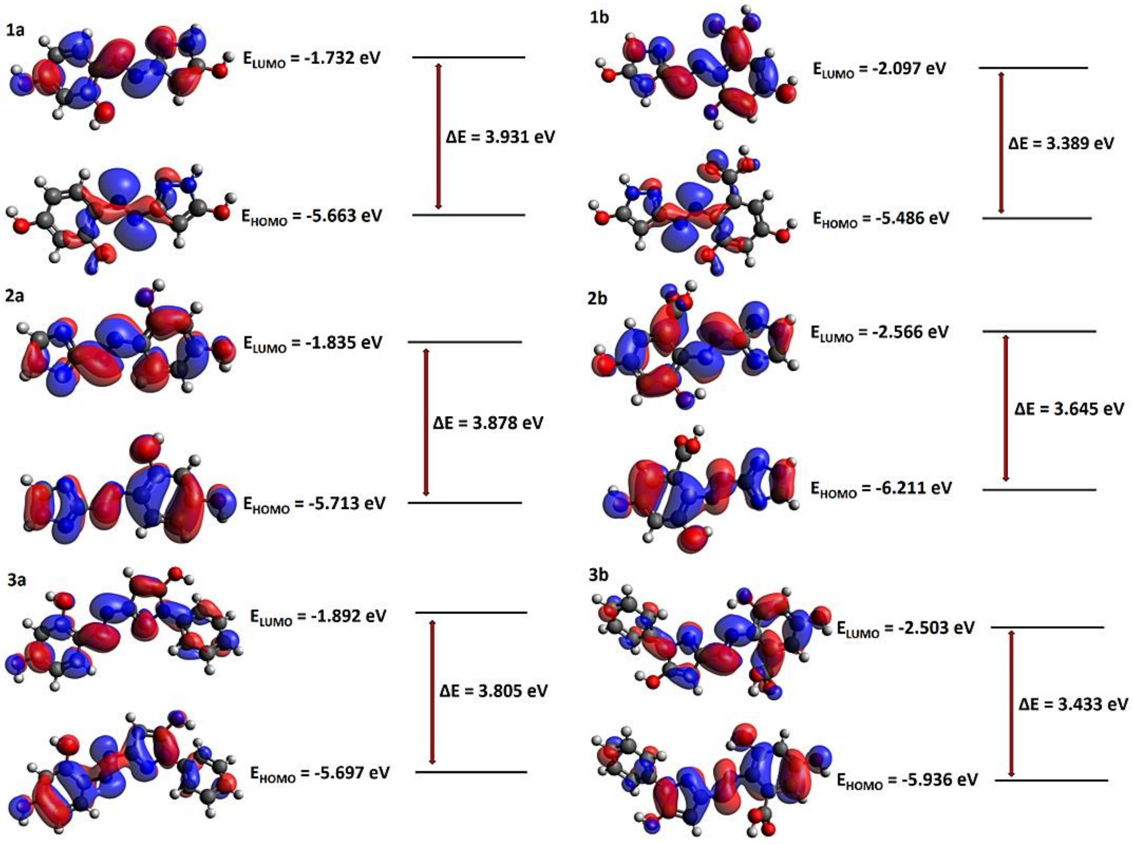

Figure 4. Molecular orbital surfaces and energy levels for the HOMO and LUMO of the **1a-b**, **2a-b** and **3a-b** calculated at the DFT/B3LYP/6-311G(d,p) level.

While it was determined that the LUMOs of the **1a-b** compounds were homogeneously distributed on the molecule, it was observed that the HOMOs of these compounds were concentrated in the center of the -N = N- double bond. However, it was observed that the HOMOs and LUMOs of other compounds (**2a-b** and **3a-b**) are homogeneously distributed over the molecules.

When the HOMOs and LUMOs energy gap values of the synthesized compounds were examined, it was calculated that **1b-3b** had lower energy than **1a-3a** analogs. The **1b-3b** molecules have an acid end and with the introduction of carboxylic acid into the structure, it softened the molecule compared to the **1a-3a** analogs and caused it to have high chemical reactivity. The molecule with the lowest HOMO and LUMO energy gap among all synthesized compounds is **1b**. Thus, compound **1b** was calculated to be the softest molecule compared to all other compounds, as it had the minimum kinetic stability and strong chemical reactivity.

4. Conclusion and Comment

Novel heterocyclic azo compounds containing phenolic groups were synthesized and characterized by spectroscopic techniques such as FT-IR, ^{1}H-NMR. Further, different solvent effects on visible region absorption spectra were investigated. Molecular geometry calculations of synthesized compounds were made with Density Functional Theory (DFT) using 6-311G (d,p) basis set and B3LYP level. Additional, HOMO-LUMO orbital calculations were carried out with the time dependent DFT (TD-DFT) approach. It was observed that hypsochromic shifts and bathochromic shifts differ in different solvents. This is thought to be due to the polarities of the compounds in disparate solvents. In addition, when the HOMO and LUMO energy gaps of the synthesized compounds were evaluated, it was determined that the **1b-3b** compounds were lower than the **1a-3a** analogs. This can be explained by the low kinetic stability and high chemical reactivity of the acid substitution in the **1b-3b** series. It was determined that **1b** was the softest compound among all synthesized compounds. It is anticipated that this study will make a significant contribution to the literature and the dyestuff industry and will form the basis for possible applications.

Author Statement

Shahodat Irmuminova: Investigation, Original Draft Writing
Barış Sezgin: Investigation, Software, Visualization, Original Draft Writing
Tahir Tilki: Project Administration, Resource/Material/Instrument Supply, Review and Editing

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Conflict of Interest

As the authors of this study, we declare that we do not have any conflict of interest statement.

Ethics Committee Approval and Informed Consent

As the authors of this study, we declare that we do not have any ethics committee approval and/or informed consent statement.

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