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Araştırma Makalesi

Synthesis and Theoretical Calculations of Benzoic Acid-Based New Mono Azo Dye

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Abstract: This study describes the synthesis, characterization and theoretical calculation of 3,5-dihydroxy-2-(naphthalen-2-yldiazenyl) benzoic acid. The synthesized compound was obtained through efficient synthetic route using 2-Naphthylamine and 3,5-dihydroxybenzoic acid as starting materials and characterized by various spectroscopic techniques such as Fouirer Transform Infrared Spectroscopy (FTIR), Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR), Carbon Nuclear Magnetic Resonance Spectroscopy (^{13}C-NMR), Ultraviolet–visible spectroscopy (UV-Vis). All theoretical calculation was performed with Density Functional Theory (DFT). Optimized molecular structure, vibrational spectra, NMR chemical shift values, frontier molecular orbitals, bond lengths (Å), bond angles (°) and Molecular Electrostatic Potential (MEP) diagram of molecule were calculated using the 6-311G(d,p) basis set. It has been observed that the results obtained from the experimental and theoretical calculations support each other and were in harmony.

Key words: Benzoic acid, Mono azo dye, Theoretical Calculation

Benzoik Asit Bazlı Yeni Azo Boyar Madde Sentezi ve Teorik Hesaplamaları

Öz: Bu çalışmada 3,5-dihidroksi-2-(naftalen-2-ildiazenil) benzoik asidin sentezi, karakterizasyonu ve teorik hesaplaması anlatılmaktadır. Sentezlenen bileşik, başlangıç malzemeleri olarak 2-Naftilamin ve 3,5-dihidroksibenzoik asit kullanılarak verimli sentetik yoldan elde edildi ve Fourier Dönüşümlü Kızılötesi Spektroskopisi (FTIR), Proton Nükleer Manyetik Rezonans Spektroskopisi (^{1}H-NMR), Karbon Nükleer Manyetik Rezonans Spektroskopisi (^{13}C-NMR), Ultraviyole-Görünür Spektroskopi (UV-Vis) gibi çeşitli spektroskopik tekniklerle karakterize edildi. Tüm teorik hesaplamalar Yoğunluk Fonksiyonel Teorisi (DFT) ile yapıldı. Optimize edilmiş moleküler yapı, titreşim spektrumları, NMR kimyasal kayma değerleri, sınır moleküler orbitalleri, bağ uzunlukları, bağ açıları ve molekülün Moleküler Elektrostatik Potansiyel (MEP) diyagramı 6-311G(d,p) temel seti kullanılarak hesaplandı. Deneysel ve teorik hesaplamalardan elde edilen sonuçların birbirini desteklediği ve uyum içinde olduğu görüldü.

Anahtar kelimeler: Benzoik asit, Mono azo boya, Teorik hesaplama

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1. Introduction

Azo dyes were used in many other branches besides the textile industry. It was frequently used in analytical and inorganic chemistry due to its color properties, stability and selectivity against different metal ions [1-5]. In addition, azo benzene derivatives are frequently used in inkjet printers, as color agents in food, in electrooptic devices, in medicine and biology due to their pharmacological and microbiological properties [6-10].

Benzoic acid and its derivatives have been well-known aromatic compound in chemistry because of their unique features. It can be found in certain proportions as an additive and preservative in various cosmetic products, medicines and foods [11-13]. It has also been reported to have antimicrobial, antifungal and antihepatotoxic activity [14-16].

Theoretical calculation, which is a research method that provides many advantages such as to be able to understand the mechanism of chemical reactions in depth, to make up for experimental deficiencies, to investigate the causes of physical events, etc., has gained more and more importance and progressed in recent years [17-20]. By means of theoretical calculation, various properties and structure-activity relationships can be obtained and predicted theoretically, thus shortening the development cycle of materials, greatly reducing the research cost in studies.

In the light of all this information, in the present study, 3,5-dihydroxy-2-(naphthalen-2-yldiazenyl) benzoic acid was synthesized by diazotization of 2-Naphthylamine and coupling with 3,5-dihydroxybenzoic acid. Its structure was characterized with UV–vis, FTIR, ^{1}H-NMR, ^{13}C-NMR and absorption properties. As theoretical, we focused on the calculation of optimized molecular structure, vibrational spectra, proton and carbon NMR chemical shift values, frontier molecular orbitals, bond lengths (Å), bond angles (°) and MEP diagram of the mono azo dye by using B3LYP method at 6-311G(d,p) base set. It has been observed that the results support each other and were in harmony.

2. Material and Method

2.1 Experimental equipments

The chemicals and spectroscopic grade solvents used in the study were obtained from Sigma Aldrich and Merck Chemical Companies and were used without purification. FTIR analysis was performed with Perkin Elmer Frontier Spectrometer using KBr. NMR analysis were performed in deuterated dimethylsulfoxide (DMSO-d_6) using Varian 600 MHz NMR spectrometer and chemical shifts are reported in δ units (ppm). UV-Visible absorption spectra was recorded on Shimadzu UV-1800 spectrophotometer at the wavelength of maximum absorption (λ_{max}) of dye in dimethylsulfoxide (DMSO). Melting point was determined in open glass capillary tube by means of a BUCHI Melting Point M-565 aparatus.

2.2 Computational method

GAUSSIAN 09W package programme and the DFT based on B3LYP hybrid functional with 6-311G(d,p) basis set was used to investigate the optimized molecular structure, vibrational spectra, proton and carbon NMR chemical shift values, frontier molecular orbitals and MEP diagram of synthesized mono azo dye [21-23]. The calculated optimized structure of dye was presented in Figure 1. The chemical shift calculations for ^{1}H-NMR and ^{13}C-NMR of dye was performed with Gauge-Invariant Atomic Orbital (GIAO) method [24]. Also, highest occupied and lowest unoccupied molecular orbitals

(HOMO and LUMO) of mono azo dye were calculated by the same basis sets and computational methods.

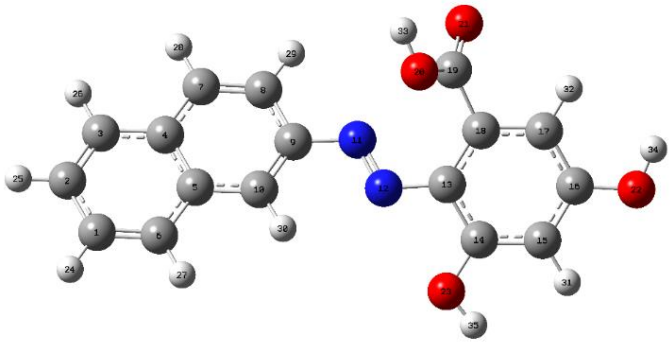

Figure 1. Optimized structure of synthesized dye

2.3 Synthesis of 3,5-dihydroxy-2-(naphthalen-2-yldiazenyl)benzoic acid

2-Naphthylamine (358 mg, 2.5 mmol, 1.00 eq) was dissolved in 5 mL concentrated HCl and 2 mL of water. The solution was cooled to 0-5°C with ice-salt bath and then a cold solution of $NaNO_2$ (190 mg, 2.75 mmol, 1.10 eq) in 2 mL water was added in a dropwise manner with constant stirring. The mixture was stirred for 1 h without increasing above 0°C and the diazonium salt was formed. 3,5-dihydroxybenzoic acid (386 mg, 2.5 mmol, 1.00 eq) and sodium acetate (410 mg, 5.0 mmol, 2.00 eq) were dissolved in 10 mL methanol and the mixture cooled to 0°C with ice-salt bath. The diazonium salt solution was added dropwise to the prepared coupling mixture and stirred at 0-5°C for 3 h. The resulting dark red solution was poured into 100 mL of ice water and pH was adjusted to 4-5 with aqueous saturated sodium acetate solution. The mixture was stirred for 1 h at 5 °C. The resulting dark red solid was filtered, washed with cold water and dried at 50°C under vacuum. Yield 709 mg, 92%, dark red solid. Melting point: 243-245°C.

The general route for the synthesis was shown in Figure 2.

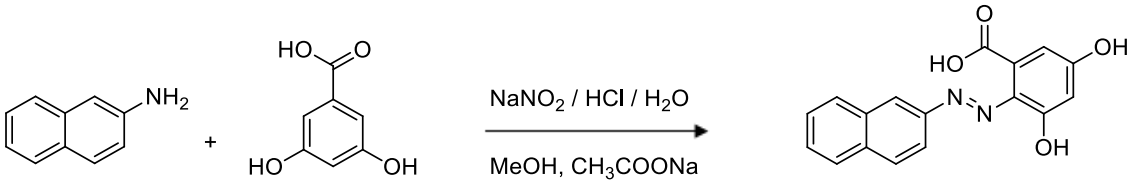

Figure 2. The general route for the synthesis

3. Results

The FTIR spectra of 3,5-dihydroxy-2-(naphthalen-2-yldiazenyl)benzoic acid showed C-H band at 1283 cm^{-1}, OH band at 3354 cm^{-1}, COOH band at 1676 cm^{-1}, C-N band at 1399 cm^{-1} and N=N band at 1478 cm^{-1}, experimentally. Theoretically, the same bands were observed at 1349, 3703, 1752, 1464 and 1501 cm^{-1}, respectively. Significant experimental and theoretical IR values of the synthesized compound were given in Table 1.

Table 1. Significant experimental and theoretical IR values of 3,5-dihydroxy-2-(naphthalen-2-yldiazenyl)benzoic acid

	Vibratioanal frequencies (cm^{-1})				
	V_{C-H}	V_{OH}	V_{COOH}	V_{C-N}	$V_{N=N}$
Experimental	1283	3354	1676	1399	1478
Theoretical	1349	3703	1752	1464	1501

The linear regression graph between experimental and theoretical FTIR frequencies was showed in Figure 3. The correlation was found y = 1.076x and R^2 = 0.9943. This correlation showed that experimental data and calculated theoretical data were compatible.

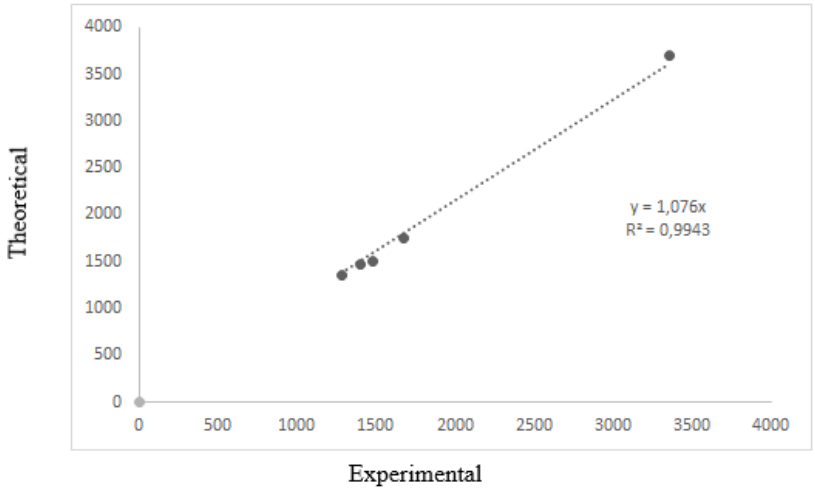

Figure 3. The linear regression graph between experimental and theoretical FTIR frequencies

Experimentally, bound to the benzoic acid ring, the proton belonging to the carboxylic acid group at 13.30 ppm and the proton from the OH groups were observed at 11.02 ppm. Also, C-H protons in the structure of benzoic acid were showed at 6.64 and 6.46 ppm. The C-H protons in the naphthalene structure were observed at 8.44, 8.08-8.06, 8.05, 8.00-7.97, 7.92, 7.62 and 7.59. Theoretically calculated with DFT/B3LYP/6- 311G(d,p), the proton of carboxylic acid showed peak at 5.76 ppm, the proton of hydroxyl groups at 4.82 and 4.95 ppm. When the C-H protons attached to the aromatic rings were examined, it was observed that they were in good agreement with the experimental data. All ^{1}H-NMR values of compound (calculated and experimental) were presented in Table 2.

Table 2. Experimentally and theoretically ^{1}H-NMR chemical shifts

H Number	Experimental	Theoretical
33H	13.30 (s, 1H, COOH)	5.76
34H or 35H	11.02 (s, 1H, OH)	4.82-4.95
30H	8.44 (d, *J*=1.9 Hz, 1H)	8.49
29H	8.08-8.06 (m, 1H)	8.31
26H	8.05 (d, *J*=8.9 Hz, 1H)	8.14
28H	8.00-7.97(m, 1H)	8.26
27H	7.92 (dd, *J*=8.8 Hz, *J*=2.00Hz, 1H)	8.24
24H-25H	7.62-7.59 (m, 2H)	7.77-7.82
32H	6.46 (d, *J*=2.5 Hz, 1H)	6.43
31H	6.64 (d, *J*=2.5 Hz, 1H)	6.66

Experimentally and theoretically calculated from DFT/B3LYP/6-311G(d,p) method ^{13}C-NMR values were given in Table 3. As can be seen from the table, all carbon atoms in the synthesized molecule resonated at similar values experimentally and theoretically.

Table 3. Experimentally and theoretically ^{13}C-NMR values

C Number	Experimental	Theoretical
19C	169.1	174.6
16C	163.0	166.4
14C	156.0	163.6
9C	148.3	153.5
13C	139.0	139.3
4C	134.4	139.1
5C	133.6	136.9
6C	130.1	135.2
8C	129.5	133.6
7C	128.8	132.9
2C	128.5	132.1
3C	128.2	131.9
1C	127.7	131.0
18C	126.4	128.4
10C	116.4	114.4
17C	108.6	111.7
15C	104.7	106.4

The experimentally absorption spectrum (UV-vis) of compound in DMSO was given in Figure 4. Also, the theoretically absorption spectrum (UV-vis) of compound was exhibited in Figure 5. When the spectra are examined, λ_{max} values of compound do not show remarkable change at experimentally and theoretically. In DMSO, the maximum wavelength was experimentally observed as 411 nm and theoretically as 484 nm.

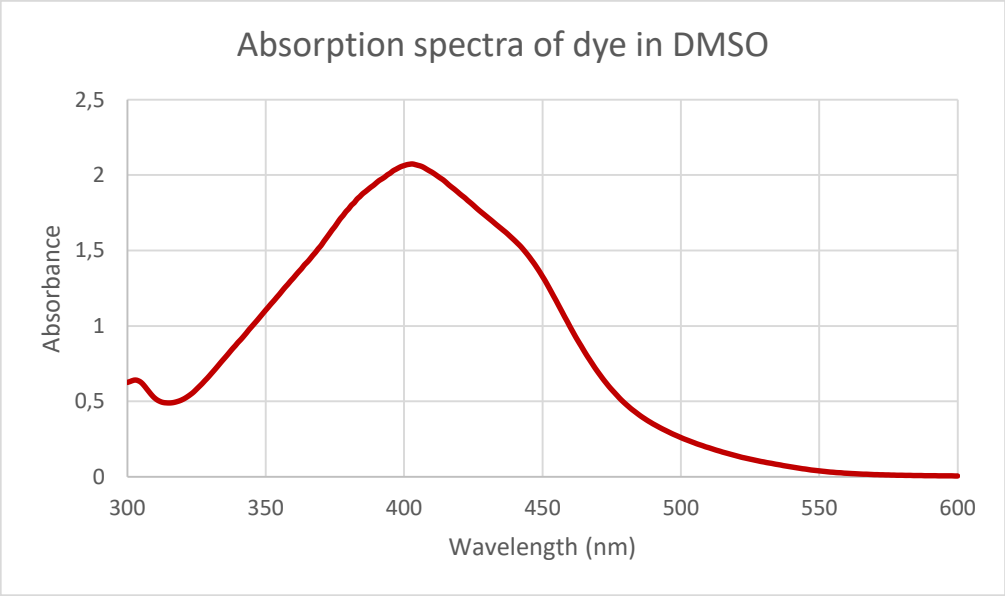

Figure 4. Experimentally UV-vis spectrum in DMSO

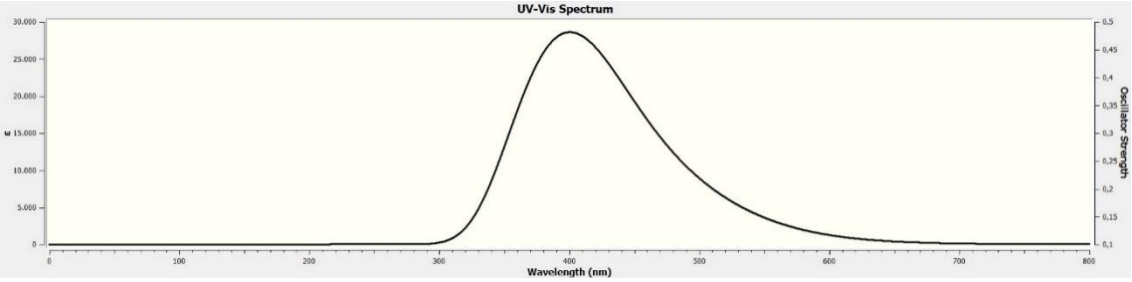

Figure 5. Theoretically UV-vis spectrum in DMSO

The HOMO and LUMO surface images of the compound were obtained at the DFT/ B3LYP 6-311G(d,p) level using the HOMOS-LUMOS Gaussian W09 package program and are given in the Figure 6. In HOMO-LUMO gaps, which are important for evaluating their effectiveness in chemical reactions, molecules with high gap energies are hard, while molecules with low gap energies are soft which are more reactive in chemical reactions. The calculated LUMO energy of the synthesized compounds was -1.3394 eV, while the HOMO energy was -5.6329 eV.

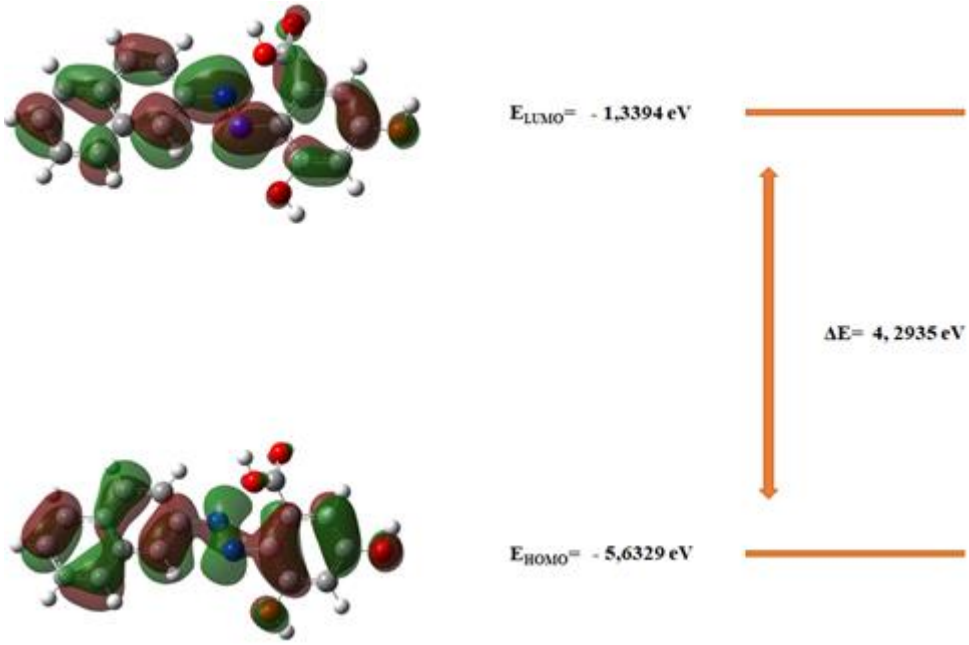

Figure 6. Molecular orbital surfaces and energy levels for the HOMO and LUMO for 3,5-dihydroxy-2-(naphthalen-2-yldiazenyl)benzoic acid computed at DFT/B3LYP/6-311G(d,p) level

The molecular electrostatic potential surface of 3,5-dihydroxy-2-(naphthalen-2-yldiazenyl)benzoic acid was calculated and its three dimensional MEP diagram was given in Figure 7. In the MEP diagram, the regions shown in red represent regions with high electron density, while the regions shown in blue represent regions with high positive charge density. In MEP diagrams, the red region provides information about the nucleophilic reactivity of the molecule, while the blue region provides information about the electrophilic reactivity of the molecule. When the MEP diagram of the synthesized molecule is examined, a high positive charge density was observed on the OH protons bound to the benzoic acid ring.

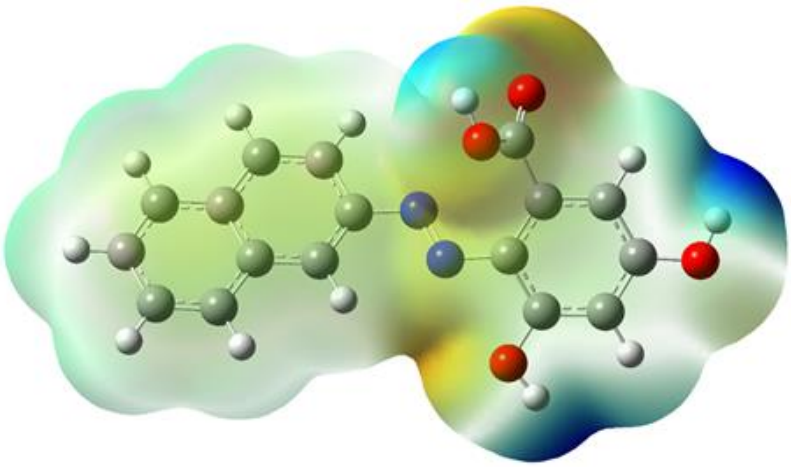

Figure 7. Three dimensional MEP diagram of 3,5-dihydroxy-2-(naphthalen-2-yldiazenyl)benzoic acid

The structural parameters, bond lengths (Å) and bond angles (°), of 3,5-dihydroxy-2-(naphthalen-2-yldiazenyl)benzoic acid were calculated using B3LYP functional with 6-311G(d,p) basis set in gas phase. In the benzoic acid structure, the bond lengths between C-O were calculated in the 1.205-1.359 Å. The dual bond length of the Azo group in the molecule is in the double bond character as expected from the structure and is calculated around 1.250 Å. At the end of the calculations, the single bond was observed approximately 1.351 Å and a double bond approximately between 1,205 Å - 1.256 Å.

When the calculated bond angles of 3,5-dihydroxy-2-(naphthalen-2-yldiazenyl)benzoic acid were evaluated, it was generally found to be 120°. The molecular geometry around the atoms was in the form of a trigonal planer. The smallest bond angle in the optimized geometry of the molecule was calculated at 112.3° between C18-C19-O20 atoms, while the largest bond at 123.1° between O20-C1-O21 atoms.

4. Conclusion and Comment

New mono azo dye, 3,5-dihydroxy-2-(naphthalen-2-yldiazenyl)benzoic acid, synthesized in this work. Its structure and spectroscopic properties have been characterized via FTIR, ^{1}H-NMR, ^{13}C-NMR and UV-vis. DFT/B3LYP method with the basis set of 6-311G(d,p) was used to verify the molecular structure and spectroscopic properties of experimentally synthesized mono azo dye. ^{1}H-NMR and ^{13}C-NMR chemical shift calculations of the dye was carried out with Gauge-Invariant Atomic Orbital (GIAO) method. Also, HOMO-LUMO energy of dye, bond lengths (Å), bond angles (°) and MEP diagram were examined.

This study showed that to make the correct assignment and to investigate the structural and vibrational properties, combined experimental and theoretical studies were very strong and useful approach.

Author Statement

Çiğdem Karabacak Atay: Methodology, Original Draft Writing, Review and Editing.

Mehmet Ulutürk: Investigation, Original Draft Writing, Review and Editing.

Acknowledgment

As the authors of this study, we declare that we do not have any support and thank you statement.

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.

Kaynakça

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