Theoretical Investigation of novel bis azo compounds using DFT

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Abstract

In this work, theoretical computations were performed using the Gaussian application. The results of theoretical calculations applying the density functional theory method (DFT) revealed that the azo group of -N=N- possesses a UV spectrum computed employing DFT-TD in the range of 250-500 nm. Several physical parameters were also calculated in this study, including Dipole moment (μ; Debye), HOMO and LUMO energies (EHOMO, ELUMO), energy gap (ΔEg in ev), ionization energy (IP in ev), electronic affinity, hardness, electronegativity, and the electrophiles (□, □, EA, ɳ, in ev), respectively.

Keywords: bis azo, dye, DFT approach, HOMO, LUMO

المستخلص

تضمنت هذه الدراسة استخدام برنامج الكاوس للاجراء الحسابات النظرية حيث تم استخدام طريقة نظرية دالة الكثافة DFT وقد اضهرت نتائج الحسابات النظرية ان المركب ثاني مجموعة الازو انه يمتلك طيف الاشعة فوف البنفسجية المحسوبة من خلال TD – DFT في مدى 250-500 nm. كما تم في هذه الدراسة حساب بعض الخصائص الفزيائية عزم ثنائي القطب (μ in Debye) ، طاقة المدارات (E_{HOMO}، E_{LUMO}) ، فجوة الطاقة (ΔEg in ev) ، طاقة التأين (IP in ev) ، الالفة الكترونية ، الصلابة ، الكهروسالبية ، اللالكتروفيلية (ω، χ، E_A، η in ev) على التوالي.

الكلمات المفتاحية: bis azo ، صبغة ، تقنية DFT ، HOMO، LUMO

1. Introduction

Current dye chemistry production is dominated by azo dyes, and potential future developments could increase their relative significance. They are essential to the functioning of the dye and printing industries. Furthermore, a straightforward process of diazotization and coupling is used to create these dyes. To achieve the desired color characteristics, productivity, and particle size of the dye for enhanced dispersibility, many approaches and modifications are employed. [1]

However, around 60% of all dyes are azo dyes, which are the most often used dyes. The functional group (-N=N-) that connects two symmetrical and/or asymmetrical identical or non-azo alkyl or aryl radicals distinguishes these molecules. [2]

Azo dyes are the most significant synthetic colorants that have been utilized extensively in the production of textiles, paints, papers, and other applications [3]. Azobenzene has been incorporated into a broad range of molecular structures, such as polymers, dendrimers, liquid crystals, self-assembled monolayers, and biomaterials, due to light-induced modifications in the azo moiety's molecular configuration and physiochemical characteristics attributed to E ⇆ Z photoisomerization. [4-5] The features of azo-functionalized molecular systems are influenced by light-driven structural modifications of the azobenzene group integrated into a greater molecule[6]. Our goal is to offer a purely hypothetical viewpoint on the optimal geometries, orbital energies (HOMO, LUMO), IR spectra, Raman scatting, and UV/Vis spectra of 4,4'-([1,1'-biphenyl]-4,4'-diylbis(diazene-2,1-diyl))dianiline as illustrated in Figure 1.

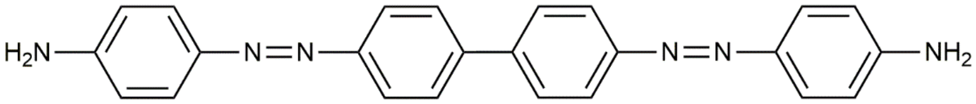


Figure.1 Chemical structure of 4,4'-{[1,1'-Biphenyl]-4,4'-diylbis[(E)diazene-2,1-diyl]}dianiline.

For use in organic light-emitting diodes, solar cells, and field-effect transistors, materials with significant electrical properties, as well as photochemical attributes, constitute fascinating candidates[7].

Application employed in the study

The DFT B3LYP functional with the 6311++g(d,p) basis set was used for the geometric optimization and frequency analysis. The Gaussian 09 software package was employed for all calculations in this work.

Results & Discussion

Outline of geometrical structures

Figure 2 displays the optimal geometries of compounds A and B as determined by the B3LYP/6-31+G(d,p) level. Figure 3 summarizes the key optimized geometric properties of compound A. Further, table 1 shows the Energies (Hartree) and their corresponding dipole moments (Debye).

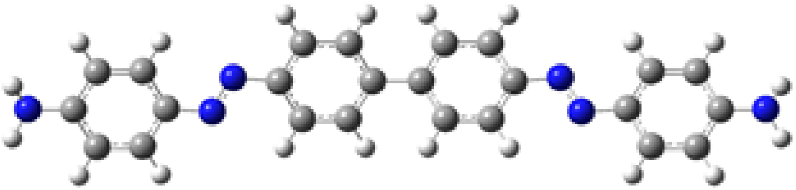
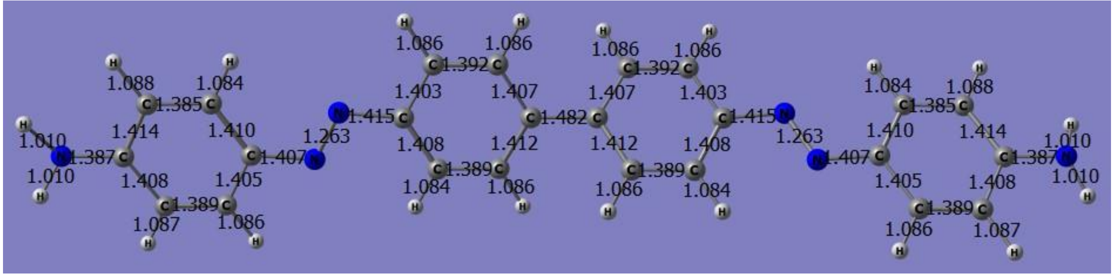
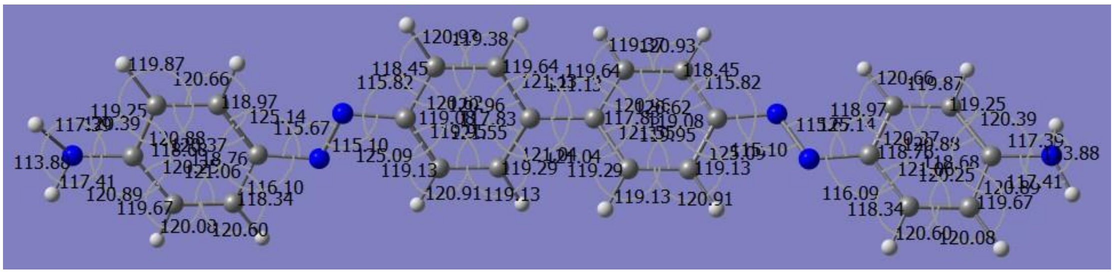


Figure 2. Compound A with optimized geometries were computed using the B3LYP/6-31+G(d,p) approach. Deep blue: N, ash: C, cyano: H

The identical widely utilized density functional theory was applied to all of the computations7.



Bond lengths for compound A in angstroms



Bond angles and dihedral angles for compound A, in degrees

Figure 3. Geometric Characteristics of Compounds A in the Ground State Optimized at B3LYP/6-31+G (d,p)

Table 1. Computed energies (Hartree), point groups, and their corresponding dipole moments (Debye), respectively

Compound	Method	E	μ	Point group
A	DFT	-1255.134975	0.96	C1

The electronic structure and excited states of the compounds A

States of excitation (λ = 250-700 nm) computation for compounds A from the Optimal Initial Geometry at B3LYP/6-31+G(d,p)

In the electronic absorption spectra of compound A, the band at λmax 455.19 nm possesses an extremely high oscillation amplitude of f = 1.988, which is indicative of

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By applying TD/DFTB3LYP/6-31+G (d,p) to calculate electronic absorption spectra, a broad and long-wavelength absorption band between 340 and 690 nm is discernible.

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Similarly, the band at 476.74 nm (S0−S1) for the n−π* transition and a second band at 476.20 nm (S0−S2) for the π−π* transition are both present. The Absorption Wavelengths λMax (nm), Excitation Energies, Eex (eV), and Oscillator Strengths (f), electronic transition, orbital symmetry-singlet (sym), Configurations Composition(corresponding transition orbitals) wave functions (Percentage of contribution obtained by (100 × c × c ×2).

Table 2. The electronic absorption spectra of compound A as determined by molecules from the optimal Initial geometry at B3LYP/6-31+G (d,p)

Compound	electronic transition	λ_{max}	Ex	configurations Composition (corresponding transition orbitals)	*f*	**sym**	Wavefunctions
A1	$S_0 \rightarrow S_1$	476.74 nm	2.6006	-0.38 (100→105) + 0.58 (101→104)	0.0	**A**	H-3→L+1 (28%)+ H-2→L (67%)
	$S_0 \rightarrow S_2$	476.20 nm	2.6036	0.58 (100→104) + - 0.39 (101→105)	=0.0022	A	H-3→L (67%)+ H-2→L+1 (30%)
	$S_0 \rightarrow S_3$	455.19 nm	2.7238	0.704 (103→104)	1.9888	A	H→L(99%)

Investigation of FMOs and Electronic Characteristics of the Compounds A

Frontier molecule orbitals (FMOs) are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which are involved in electrical features, optical characteristics, UV/Vis spectra, and chemical processes. [9]. Additionally, the electron affinity (A=-ELUMO) and ionization potential (I=-EHOMO) are connected to the EHOMO and ELUMO, respectively. The global hardness (η), electronegativity (χ), electronic-chemical potential (μ) and electrophilicity (ω), chemical softness (S) parameters are computed with the following formulas: η=I-A/2), (χ=I+A/2), (μ=-(I+A)/2), (ω=μ2/2η), (S=1/2η) [10]. The electrical characteristics of compounds A and FM analysis were employed. In addition, the electrical parameters of compounds A were computed utilizing B3LYP/6-31+G(d,p)

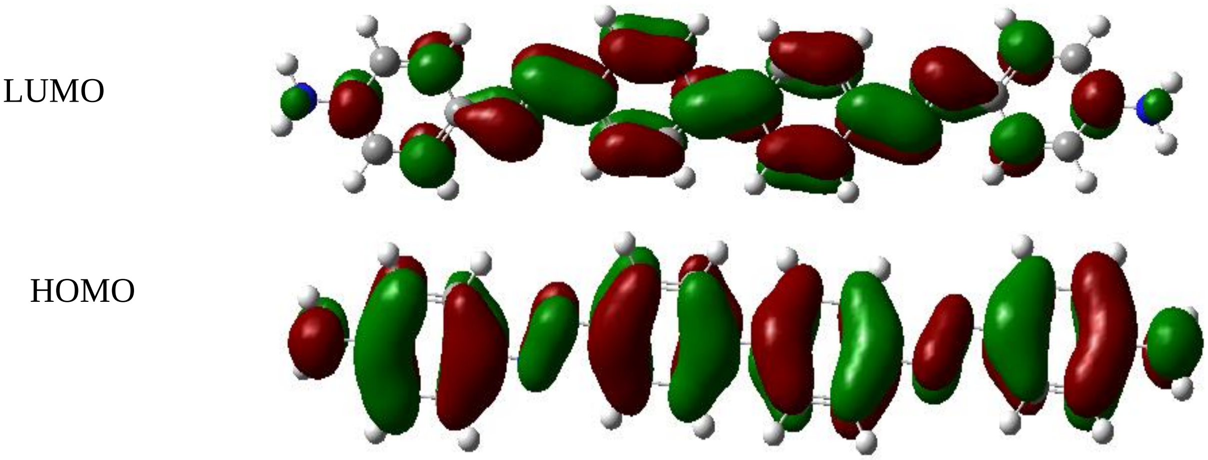
Table 3. Electronic parameters of the Compounds A

Property	A
E_{HOMO}(eV)	-5.43
E_{LUMO}(eV)	-2.42
Eg (eV)	3.01
I(eV)	5.43
A(eV)	2.42
χ(eV)	3.925
η(eV)	1.505
μ(eV)	-3.925
ω(eV)	5.11
S(eV)	0.33

Energy levels for HOMO, LUMO, and the energy gap between them, Eg (HOMO-LUMO), which is a mathematical expression that describes the molecular orbital, are shown in Table 5. In total, model compound A possesses 140 alpha orbitals, 73 of which are occupied whereas the remaining 67 are purely fictitious. Orbital 73 stands for HOMO orbitals, while orbital 74 stands for LUMO orbitals. According to our findings, HOMO and LUMO have respective energy levels of -11.62 and -11.5 eV.

Table 5: DFT approach at B3LYP/ 6-31G(d) level yielded the calculated HOMO-LUMO energy (ev) and HOMO-LUMO band gap Eg values for compound A.

compound	HOMO	LUMO	ΔEg
A	-11.62	-11.5eV	0.12



(Figure 4**)** The highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of bis azo compounds.

Molecular Electrostatic Potential (MEP)

Figure 5 displays the ESP on the molecular surface. It is beneficial to investigate a molecule's chemical reactivity negative areas. The negative and positive values of the ESP, which has a range of -9.33 to +9.33 au, are represented by the colors red and blue, respectively. The maximum attraction is indicated by blue, whereas the strongest repulsion is indicated by red.

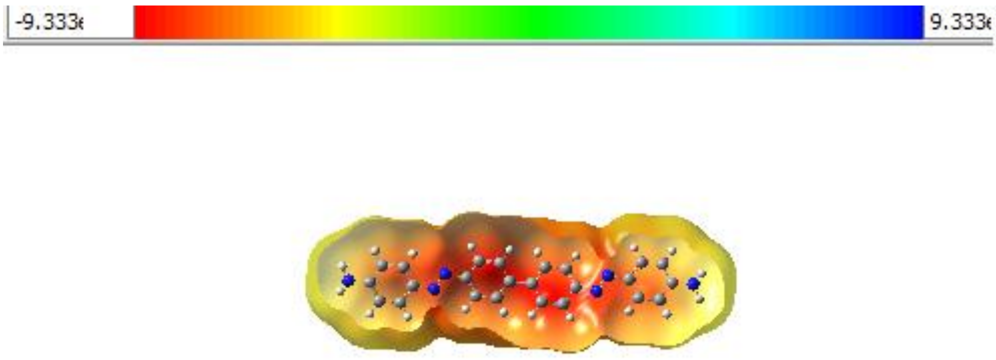


Figure .5 Electrostatic potential (ESP) of Compounds A.

Conclusions

Studies on molecular geometry and electrical behavior are essential for comprehending the azo -N = N- structure. The DFT using B3LYP functional and the 6-31+G(d,p) basis set was applied to predict the molecular electrostatic potential and excited states. To investigate the electronic properties, UV/Vis spectra, excitation energies and the maximum absorption wavelength, oscillator strength, HOMO, LUMO energies, and the energy difference between them, Eg (HOMO-LUMO), electronic transitions, and transition probabilities for compounds A, TD-DFT calculations utilizing B3LYP/6-31+G(d,p) in the gas phase were conducted

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