Quantum Chemical Modeling, Synthesis, Spectroscopic (FT-IR, Excited States, UV/Vis) Studies, FMO, QTAIM, NBO and NLO Analyses of Two New Azo Derivatives

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Highlights

- Two new azo derivatives were synthesized and FT-IR, UV-Vis and NMR spectra were • measured
- Detailed structural, physical and chemical properties were studied •
- Hyperpolarizability calculations reveal suitability for optoelectronic and photonic • applications

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Quantum Chemical Modeling, Synthesis, Spectroscopic (FT-IR, Excited States, UV/Vis) Studies, FMO, QTAIM, NBO and NLO Analyses of Two New Azo Derivatives

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ABSTRACT

In this research, we report the results of experimental and density functional theory (DFT)/time-dependent DFT analyses of two new azo derivatives that absorb light in the visible range: (E)-2-((4-(diethylamino)phenyl)diazenyl)-6-methoxy-3methylbenzo[d]thiazol-3-ium (I) and N,N-diethyl-4-((6-methoxybenzo[d]thiazol-2yl)diazenyl)aniline (II) in the presence of water (I) and chloroform (II). The molecular geometry and excited states of the compounds were investigated, and their natural bond orbital, frontier molecular orbital, quantum theory of atoms in molecules, and nonlinear optical (NLO) parameters were calculated. In addition, Fourier-transform infrared, nuclear magnetic resonance, and ultraviolet/visible spectral parameters were generated from the derived structures and compared to experimental spectral parameters. The practical applicability of the azo derivatives was investigated by determining their electronic and NLO properties, which demonstrated that both molecules have potential for optoelectronic and photonic applications. A high degree of approximation between the calculated and experimental results was demonstrated.

Keywords: Optoelectronics; NLO; UV/Vis spectroscopy; NBO

1. INTRODUCTION

Hydrazones are a class of organic compounds with the structure R1R2C=NNH₂. The chemistry of the carbon–nitrogen double bond of hydrazones provides the backbone for condensation reactions in benzo-fused *N*–heterocycles [1]. Hydrazones containing azomethine groups are an important class of compounds for new drug development [2,3]. Many researchers synthesized these compounds and evaluated their various biological activities. Hydrazides/hydrazones act as antibacterial, antiviral, analgesic and anti-inflammatory, anti-platelet, vasodilator, anticonvulsant, antioxidant, diuretic, antimalarial, anti-arthritis, and anti-trypanosomal agents, as well as hormone antagonists and receptor

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agonists [3,4]. They can also be integrated in liquid crystal displays, solar cells, and optoelectronics devices due to their conjugated donor–acceptor network and excellent nonlinear optical (NLO) properties [5-7]. Thus, we synthesized two azo derivatives and compared the results of quantum chemical calculations with experimental data to investigate their potential for optoelectronic and photonic applications.

2. METHODS

2.1 Experimental methods

All materials and reagents were commercially available and used without further purification to synthesize the azo derivatives (E)-2-((4-(diethylamino)phenyl)diazenyl)-6-methoxy-3-methylbenzo[d]thiazol-3-ium (I) and N,N-diethyl-4-((6-methoxybenzo[d]thiazol-2-yl)diazenyl)aniline (II), abbreviated hereafter as GSL and GSL-1, respectively (Scheme 1).



To synthesize GSL-1, a solution of 2-amino-6-methoxybenzothiazole (0.2 mol) in sulfuric acid (50 %, 400.0 mL) was heated to 95 °C until completely dissolved and then cooled to -2 °C. The solution was added by dropping sodium nitrite (0.2 mol, 100.0 ml) aqueous solution with a temperature of -5–0 °C. The resulting mixture was stirred at -5–0 °C for 1 h. A sulfuric acid (40%, 94.0 mL) solution of N, N-diethylaniline (0.207 mol) was added to the reaction mixture. The reaction proceeded at 30 °C for 2 h, and the products were then filtered and dried to obtain the solid **GSL-1**. Yield: 80.79 %; melting point: 145–

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147 °C.

To synthesize GSL, GSL-1 (1.0 mol), zinc oxide (1.0 mol), and water (250.0 mL) were added to a 2.0 L round bottom flask. After stirring for 30 min, dimethyl sulfate (3.0 mol) was added dropwise to the reaction mixture. The reaction proceeded at 30 °C for 6 h, and then the mixture was filtered under suction to remove the solvent from the filtrate. The solid was dissolved in chloroform, and the undissolved matter was removed by filtering. Zinc chloride (1.2 mol), concentrated hydrochloric acid 32% (180.0 g), and water (600.0 mL) were added into the reaction mixture. The reaction proceeded at 60 °C for 6 h, and then sodium chloride (600.0 g) was added, followed by cooling to 45 °C, filtering, and drying to obtain the dark solid **GSL**. Yield: 99.8 %; melting point: 195–197 °C.

GSL and GSL-1 were analyzed using various spectroscopic methods. Nuclear magnetic resonance (NMR) spectra were measured using a Bruker Avance AV II-400 MHz instrument. Fourier-transform infrared (FT-IR) spectra were recorded using an IR Affinity-1 infrared spectrometer with the KBr pellet method. Ultraviolet-visible (UV-Vis) absorption spectra were measured using a Cary 60 UV-Vis scanning spectrophotometer in H₂O and CHCl₃, for GSL and GSL-1, respectively. These solvents were used in all analyses, unless stated otherwise.

2.2 Computational methods

Quantum chemical calculations of the GSL and GSL-1 structures were performed using the density functional theory (DFT) method with the Amsterdam density functional (ADF) modeling suite [8,9]. Conformational analysis was used to locate the conformation with the lowest energy followed by geometry optimization, and calculations of the IR spectra [10], molecular electrostatic potential (MEP), and frontier molecular orbital (FMO) of GSL and GSL-1 in H₂O and CHCl₃, respectively, using the GGA:OPBE XC functional with a TZP Slater basis-set [11]. In addition, a TZ2P Slater basis-set was used for the quantum theory of atoms in molecules (QTAIM) calculations. The COSMO solvent model [12], using Klamt radii with no geometric constraints, was used for all calculations. Scalar relativistic effects

were incorporated via the ZORA formalism [13–15], except for the QTAIM calculations, due to incompatibility issues in ADF. Furthermore, time-dependent DFT (TD-DFT) excited-state calculations [16] were conducted with a TZ2P basis-set, while NMR calculations [17] were conducted with a TZ2P-J basis-set for GSL and GSL-1 in H₂O and CHCl₃, respectively. These solvents were used in all analyses, unless stated otherwise. The first 20 excited states were determined via the Davidson method for spin– orbit (perturbative) singlet and triplet states [18]. The ¹H and ¹³C NMR chemical shift values were determined considering perturbative spin–spin coupling [19]; however, only chemical shifts without coupling assuming chemically non-equivalent regions are reported. Natural bond orbital (NBO) [20] and NLO analyses were conducted using the Gaussian 09W program [21] and the Cam-B3LYP/6-31(d,p) level of theory for GSL and GSL-1 using the C-PCM solvent model coupled to universal-force-field radii.

3. RESULTS AND DISCUSSION

3.1 Optimized structures of GSL and GSL-1

The computational studies gave optimized molecular structures of GSL and GSL-1, as illustrated in Fig. 1. with DFT-calculated bond lengths and angles of selected atoms listed in Table 1.



Fig. 1. Optimized molecular structures of GSL and GSL-1

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		GSL		GSL-1					
	Bond		Bond angle		Bond		Bond		
Parameter	length (Å)	Parameter	(°)	Parameter	length (Å)	Parameter	angle (°)		
O1–C2	1.352	01C2C7	124.2	O1–C2	1.359	01–C2–C7 C4–C5–	124.2		
O1–C19	1.428	C4-C5-N21	127.8	O1–C19	1.423	N20 C5–N20–	125.7		
C5-N21	1.399	C5-N21-C8	113.4	C5-N20	1.407	C8	110.1		
C6-S25	1.734	C6-S25-C8	90	C6-S24	1.728	C6-S24–C8	88		
C8-N21	1.346	C7–C6-S25	126.5	C8-N20	1.309	C7–C6-S24 C8–N21–	127.6		
C8-N22	1.343	C8–N22–N23 C11–C12–	109.8	C8-N21	1.371	N22 C11–C12–	111.6		
C8-S25	1.738	N24 C13–C12–	121.5	C8-S24	1.779	N23 C13–C12–	121.8		
C9-N22	1.35	N24 C15–N24–	121.4	C9-N21	1.376	N23 C15–N23–	121.7		
C12-N24	1.348	C16	115.1	C12-N23	1.369	C16	116.9		
C15-N24	1.464	C19-O1–C2	118.2	C15–N23	1.46	C19-O1–C2 N21–N22–	118.1		
C16–N24 N22–N23	1.464	N22-N23-C9	117.7	C16–N23	1.46	C9	117.1		
						N20-C8-			
	1.306	N21–C8–N22	123.4	N22–N23	1.283	N21	122.9		
C20-N21	1.456	C8-N21-C20	123.5						

Table 1. Selected optimized geometric parameters of GSL and GSL-1

3.2 Vibrational analysis

The IR vibrational spectra of GSL and GSL-1 were calculated using OPBE/TZP level of theory. GSL consists of 48 atoms which show 138 normal modes of IR active vibrations. In the spectra, main peaks were observed at 1000–1650 cm⁻¹ with higher intensity than those of GSL-1 in the C–N stretching region (1100–1660 cm⁻¹) due to the additional C–N bond. Minor peaks were observed at 2900–3200 cm⁻¹ corresponding to CH₃ stretching, and a 600–900 cm⁻¹ fingerprint region. The peaks extracted from the theoretical IR spectrum were in good agreement with those from the experimental FT-IR spectrum (Table 2). GSL-1 consists of 44 atoms which undergo 126 normal modes of IR active vibrations, with main peaks at 1100–1660 cm⁻¹ with approximately equal intensity for GSL and GSL-1, minor peaks at 2900– 8

 3200 cm^{-1} corresponding to CH₃ stretching, and a 600–900 cm⁻¹ fingerprint region. As for GSL, the peaks from the theoretical IR spectrum were in good agreement with those from the experimental FT-IR spectrum (Table 2).

Table 2. Experimental and theoretical vibrational frequencies of GSL and GSL-1 and their peak

	C	SSL			(GSL-1	
v_{exp} (cm ⁻	1			v_{exp} (cm ⁻	V _{cal}		
1)	v_{cal} (cm ⁻¹)	I _{IR}	Assignment	1)	(cm^{-1})	I _{IR}	Assignment
617.22w	615	13.1	τC–H(arom)	623.01w	652	14.48	τC –H(arom)
732.95w	735	119.42	vC-S–C sym,	740.67w	738	53.62	vC-S–C sym,
			τC–H(arom),				τ C–H(arom),
			$\beta C = C(arom)$				$\beta C = C(arom)$
827.46w	836	257.7	vC-S–C	825.53w	834	65	vC-S-C
			asym, τC–				asym, τC–
			H(arom),				H(arom),
			$\beta C = C(arom)$				$\beta C = C(arom)$
862.18w	872	157.55	$\beta C = C(arom)$	1053.13m	1058	155.86	vC-O, ωC–
							H(arom),
							$\omega C - H(CH_3)$
1004.91w	1008	208.09	$\beta C = C(arom),$	1076.28m	1068	94.48	β C–H(arom),
			vC–N				$\omega C - H(CH_3)$
1072.42m	1063	212.7	vC-O, ωC–	1134.14s	1127	665.47	β C–H(arom),
			H(arom),				vC–N, ωC–
			ω C–H(CH3)				H(CH3)
1126.43m	1129	262.74	β C–H(arom),	1228.66m	1222	503.27	β C–H(arom),
			vC–N				vC–N, vC-O
1153.43s	1146	468.11	β C–H(arom),	1255.66m	1260	509.45	β C–H(arom),
			vC–N				vN=N,
							vC=C, vC-O,
							ωC–H(CH3),
							vC–N
1172.72s	1162	716.67	$\beta C-H(arom),$	1307.74m	1313	157.73	β C–H(arom),
			vC–N, ωC–				vC–N,
			$H(CH_3)$				vC=C, ωC–
		100 50		1000 01	10.50		$H(CH_3)$
1205.51m	1215	180.53	$\beta C - H(arom),$	1332.81m	1352	111.46	$\beta C-H(arom),$
			vC–N, vC-O				vC–N,
							$vC=C, \omega C-$
1040.02	1059	70 74	N N OC	1244 20	1200	026 57	$H(CH_3)$
1240.25m	1238	12.14	$v_{1} = v_{1}, p_{-}$	1344.38m	1389	930.37	VIN=IN,
							$v \in U$. $v \in N$

assignments

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							thiazol, βC– H(arom), βC– H(CH3),vC– N
1263.37s	1270	2059.83	βC–H(arom), vC–N, vC=C, vC-O	1406.11w	1415	111.7	vC=C, vC=N thiazol, βC– H(CH3),vC– N
1288.45m	1279	125.12	βC–H(arom), vC=C, vC- O,vC–N, ωC–H(CH ₃), N=N	1490.97m	1507	805.02	vC=C asym, vC=N thiazol, βC– H(CH ₃),vC– N
1327.03m	1306	3524.26	βC–H(arom), vC–N, vC=C, ωC–H(CH ₃), vN=N	1593.2s	1616	1517.97	vC=N thiazol, vC=C asym
1344.38m	1337	506.77	β C–H(arom), vC–N, vC=C, ω C–H(CH ₃)	2370.51w	-	-	vCO ₂ (air)
1365.6m	1354	1082.42	β C–H(arom), vC–N, vC=C, ω C–H(CH ₃), vN=N	2931.8w	2985	103.22	vC– H(CH ₃)sym
1402.25w	1395	104.3	vN=N, vC=C, vC=N thiazol, β C– H(arom), ω C– H(CH ₃),vC– N	2974.23w	3012	187.52	vC– H(CH ₃)sym
1427.32m	1420	383.17	vC=C, vC=N thiazol, βC– H(CH ₃),vC– N				
1458.18w	1435	175.45	vC=C, vC=N thiazol, βC– H(CH ₃),vC– N				
1481.33w	1487	158.04	vC=C asym, vC=N thiazol, βC– H(CH ₃),vC– N				
1543.05m	1530	103.85	vC=C asym,				

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			vC=N	
			thiazol, βC –	
			H(CH ₃),vC–	
			Ν	
1558.48m	1553	256.7	vC=C asym,	
			vC=N	
			thiazol, βC–	
			H(CH ₃),vC–	
			Ν	
1595.13m	1591	58.6	vC=C asym,	
			vC=N thiazol	
1608.63s	1615	1655.12	vC=N	
			thiazol, vC=C	
			asym	<u>с</u>
2370.51w	-	-	vCO ₂ (air)	
2978.09w	2996	82.26	vC-	
			H(CH ₃)sym	

 I_{IR} , IR intensity; v, stretching; β , in plane bending; ω , out of plane bending (wagging); τ , torsion; asym, asymmetric; sym, symmetric; arom, aromatic; w, weak; m, medium; s, strong

3.3. Molecular electrostatic potential maps

MEP maps were calculated using OPBE/TZP level of theory. The total electron density mapped with an electrostatic surface is illustrated in Fig. 2, while the contour map of the electrostatic potential is illustrated in Fig. 3. In MEP maps, the negative sites with high electron density (which are prone to electrophilic attack) are shown in red, orange, and yellow, whereas the positive sites (which are prone to nucleophilic attack) are shown in blue [22]. According to the MEP maps, the regions prone to electrophilic attack in both GSL and GSL-1 are the azo region and the oxygen atoms (including N20 in GSL-1 and excluding methylated N21 in GSL). The regions prone to nucleophilic attack are the hydrogen atoms on methyl carbon atoms including N24 in GSL and N23 in GSL-1.



Fig. 2. Total electron density mapped with electrostatic surface GSL, GSL-1



Fig. 3. Contour map of electrostatic potential GSL, GSL-1

3.4. Electronic structure and excited states

Twenty excited states of GSL and GSL-1 were calculated using OPBE/TZ2P level of theory, where the nearly forbidden excitations $f \approx 0$ were ignored [23].

GSL. According to our calculations, the optimal transitions are at $\lambda = 662.99$ nm (f = 1.4520) S₀ \rightarrow S₁ with single orbital contributions (94 \rightarrow 95) 92.6% and (92 \rightarrow 95) 6.5%. In addition, a transition was observed at $\lambda = 498.16$ nm (f = 0.1771) S₀ \rightarrow S₃ with single orbital contributions (92 \rightarrow 95) 74.1%, (91 \rightarrow 95) 19.3%, and (94 \rightarrow 95) 4.2%. Moreover, a transition is apparent at $\lambda = 433.18$ nm (f = 0.1675) S₀ \rightarrow S₄ with single orbital contributions (91 \rightarrow 95) 77.6%, (92 \rightarrow 95) 14.9%, (94 \rightarrow 95) 2.1%, and (94 \rightarrow 98) 1.8%, in addition to a lower probability transition at $\lambda = 328.98$ nm (f = 0.0524) S₀ \rightarrow S₆ with single orbital contributions (94 \rightarrow 96) 89.2%, (92 \rightarrow 96) 3.5%, (89 \rightarrow 95), 1.5%, (94 \rightarrow 97) 1.2%, and (94 \rightarrow 98) 1.1%. Excitation of an electron from (94 \rightarrow 95) molecular orbital gives the main contribution to the absorption band at 662.99 nm in the visible region of the spectrum (Table S1). The theoretical excitation spectrum is in good agreement with the experimental UV-Vis absorption spectra of GSL in water $(1 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1})$. (Fig. 4.)



Fig. 4. Experimental UV-Vis absorption spectra of GSL (a) and GSL-1 (b).

GSL-1. According to our calculations, the optimal transitions are at $\lambda = 585.81$ nm (f = 1.5491) S₀ \rightarrow S₁ with single orbital contributions (90 \rightarrow 91) 96.1% and (88 \rightarrow 91) 2.4%. In addition, a lower probability transition is observed at $\lambda = 332.76$ nm (f = 0.0955) S₀ \rightarrow S₇ with single orbital contributions (90 \rightarrow 92) 46.5%, (90 \rightarrow 93) 42.7%, (86 \rightarrow 91) 4.3%, and (88 \rightarrow 93) 3.3%. Moreover, an additional lower probability transition is apparent at $\lambda = 306.97$ nm (f = 0.0946) S₀ \rightarrow S₉ with single orbital contributions (84 \rightarrow 91) 88.2%, (83 \rightarrow 91) 2.9%, (90 \rightarrow 96) 2.5% and (88 \rightarrow 94) 1.2%, in addition to a transition at $\lambda = 429.81$ nm (f = 0.0561) S₀ \rightarrow S₄ with single orbital contributions (87 \rightarrow 91) 51.6%, (88 \rightarrow 91) 40.4%, (90 \rightarrow 94) 4.2%, and (90 \rightarrow 91) 1.7%. Excitation of an electron from (90 \rightarrow 91) molecular orbital gives the main contribution to the absorption band at 585.81 nm in the visible region of the spectrum (Table S2). The theoretical excitation spectrum is in good agreement with the experimental UV-Vis absorption spectra of GSL-1 in CHCl₃ (1×10⁻⁶ mol·L⁻¹) (Fig. 4.)

3.5. FMO analysis and electronic properties

The electronic properties of GSL and GSL-1 were deduced from FMO analysis using OPBE/TZP level of theory. The results are shown in Table 3 and Fig. 5. The figures show that the highest occupied

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molecular orbital (HOMO) orbitals of GSL and GSL-1, respectively, are relatively localized throughout the molecule with the exception of some single bond (-C-C-), and sulfur in the case of GSL-1. However, the lowest unoccupied molecular orbital (LUMO) orbitals are mainly concentrated around double bonds (-C=N-, -N=N-), the double bond (-C=C-) of one of the phenyl rings, the single bond (-C-N-), and sulfur atoms.



Fig. 5. (a) HOMO and (b) LUMO of GSL. (c) HOMO and (d) LUMO of GSL-1

The HOMO and LUMO energy levels (E_{HOMO} and E_{LUMO} , respectively) are related to the ionization potential ($I = -E_{\text{HOMO}}$) and the electron affinity ($A = -E_{\text{LUMO}}$). The global hardness (η) is defined as the resistance of an atom or a group of atoms to charge transfer. The electronegativity (χ) is a measure of the power of an atom or a group of atoms to attract electrons. The electronic potential (μ) is a measure of the tendency of electrons in an atom or a group of atoms to escape its ground state. The chemical softness (S) measures the capacity of an atom or group of atoms to receive electrons. Here, η , χ , μ , ω , and S were calculated using the following equations [24]. GSL had a smaller energy gap (E_g) and η than GSL-1. Therefore, GSL is a softer molecule with higher reactivity and lower kinetic stability than GSL-1. In addition, GSL is more electronegative and electrophilic than GSL-1, with a higher tendency of accepting electrons.

$$\eta = I - A/2$$

$$\chi = I + A/2$$

$$\mu = -(I + A)/2$$

$$\omega = \mu^2/2\eta$$

$$S = 1/2\eta$$

Table 3. Calculated electrical parameters of GSL and GSL-1

Property	GSL	GSL-1
Bond energy		
(eV)	-293.009	-276.902
$E_{\rm HOMO}~({\rm eV})$	-5.352	-4.826
$E_{\rm LUMO}~({\rm eV})$	-3.922	-3.3235
$E_{\rm g}({\rm eV})$	1.43	1.5025
I (eV)	5.352	4.826
<i>A</i> (eV)	3.922	3.3235
χ (eV)	4.637	4.07475
η (eV)	0.715	0.75125
μ (eV)	-4.637	-4.07475
ω (eV)	15.0362	11.05064
<i>S</i> (eV)	0.699301	0.665557

3.6 QTAIM analysis

QTAIM analysis was conducted using OPBE/TZ2P level of theory to determine the nature of chemical bonding in GSL and GSL-1. The following results were calculated at the bond critical points (BCPs) of selected bonds, as listed in Table 4, where the electron density $p(\mathbf{r})$ describes the strength of a chemical bond, the Laplacian electron density $\nabla^2 p(\mathbf{r})$ determines where the electronic charge is locally concentrated or depleted, and the ellipticity of the electron density ε provides a quantitative assessment of the anisotropy of the electron density [25]. The molecular graphs containing BCPs are illustrated in Fig. 6. The results revealed two hydrogen-hydrogen bonds in GSL and GSL-1 with low $p(\mathbf{r})$ and positive $\nabla^2 p(\mathbf{r})$ values, which is an indication of noncovalent interactions. In addition, the hydrogen-hydrogen bonds exhibit an ε value that suggests a higher density delocalization of their interaction. Moreover, the O1–C19 bond has the lowest ε amongst the selected bonds in GSL and GSL-1. The strongest bond according to QTAIM analysis is azo N22–N23 and N21–N22 in GSL and GSL-1, respectively, with a negative $\nabla^2 p(\mathbf{r})$ indicating covalent interactions. The azo bond in GSL-1 is stronger than that in GSL, which is consistent with the shorter N=N bond in GSL-1. The additional methyl group C20–N21 in GSL reduces the strength of C8–N21 and C5–N21 relative to C8–N20 and C5–N20 in GSL-1, and also increases ε relative to C8–N20 and C5–N20 in GSL-1.

	G	SL			G	SL-1	
	<i>p</i> (r)	$\nabla^2 p(\mathbf{r})$			<i>p</i> (r)	$\nabla^2 p(\mathbf{r})$	
Bond	(a.u.)	(a.u.)	E (a.u.)	Bond	(a.u.)	(a.u.)	<i>ɛ</i> (а.и.)
O1–C19	0.24648	-0.46896	0.0017	O1-C19	0.250959	-0.49525	0.0052
O1–C2	0.298893	-0.59687	0.0586	O1-C2	0.293305	-0.58175	0.0565
C6-S25	0.206177	-0.35642	0.1760	C6-S24	0.208023	-0.36399	0.1830
C8-S25	0.206204	-0.35567	0.0276	C8-S24	0.190324	-0.27486	0.2380
C5-N21	0.299356	-0.82441	0.1520	C5-N20	0.320493	-0.93565	0.1080
C8-N21	0.332773	-0.99996	0.2610	C8-N20	0.366412	-1.15578	0.2250
C8–N22 N22–	0.35103	-1.08907	0.1670	C8–N21 N21–	0.329434	-0.98772	0.1460
N23	0.407259	-0.87041	0.0949	N22	0.431255	-0.98886	0.1170
C9–N23 C12–	0.334148	-1.01096	0.1670	C9–N22 C12–	0.31861	-0.93703	0.1350
N24 H30–	0.327912	-0.95872	0.1820	N23 H29–	0.313662	-0.90906	0.1720
H36 H31–	0.015483	0.060196	0.9320	H35 H30–	0.018115	0.064499	0.6080
H34 C20–	0.015348	0.059449	0.8930	H33	0.017843	0.063507	0.5970
N21	0.251629	-0.59473	0.0246				

Table 4. Calculated topological parameters at the BCPs of selected bonds of GSL and GSL-1



Fig. 6. QTAIM topological map with BCPs and contour electron density of (a) GSL and (b) GSL-1

3.7 NMR analysis

The ¹H and ¹³C NMR chemical shifts of GSL and GSL-1 were calculated using OPBE/TZ2P-J level of theory. The experimental ¹H chemical shifts of GSL and ¹H and ¹³C NMR chemical shifts of GSL-1 are compared.

GSL. The predicted ¹H chemical shifts for all hydrogen atoms on both phenyl rings, namely H26, H27, H28, H29, H30, H31, and H32 are 7.9302, 8.4008, 8.1333, 8.4549, 7.9022, 7.9317, and 8.6351 ppm, respectively. The chemical shifts of hydrogen atoms H33, H34, H35, H36, H46, H47, and H48 on C20, C15, and C16 that are bound to N21 and N24 are 3.8758, 4.3262, 3.8770, 4.3256, 5.5738, 3.9280, and 3.9775 ppm respectively. The high chemical shift of H46 in equivalent region of H46, H47, and H48 is due to hydrogen bonding with H32. The chemical shift for hydrogen atoms H37, H38, H39, H40, H41, and H42 on C17 and C18 are 1.5893, 1.6732, 1.4672, 1.6422, 1.6505, and 1.4632 ppm, respectively. The chemical shifts of C19 bonded to O1 are 4.6665, 4.1424, and 4.1421 ppm respectively. Although the theoretical chemical shifts showed a downward shift compared to experimental values, they were in relatively good agreement with experimental ¹H NMR (400 MHz, D₂O) δ (ppm): 7.21

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(b, 1H), 6.99-7.01 (d, J=8.4 Hz, 1H), 6.89 (b, 1H), 6.78 (b, 1H), 6.47 (b, 4H), 3.75 (s, 6H), 3.70 (s, 4H), 1.24 (b, 6H).

Furthermore, the predicted ¹³C chemical shifts for all carbon atoms on both phenyl rings, namely C2, C3, C4, C5, C6, C7, C9, C10, C11, C12, C13, and C14 are 161.2172, 120.2606, 116.0847, 135.3127, 131.6228, 104.5784, 147.1176, 141.5555, 117.2259, 153.7163, 119.3396, and 121.1767 ppm, respectively. The higher chemical shifts on C2, C9, and C12 are due to de-shielding by neighboring oxygen and nitrogen atoms. The chemical shift of C8 in thiazole is 174.5153 ppm, which is the most-de-shielded carbon in GSL. The chemical shifts of shielded carbon atoms C15, C16, and C20 bound to N21 and N24 are 48.2822, 48.3885, and 34.8636 ppm, respectively. In addition, the chemical shifts of C17 and C18 bound to C15 and C16 are 11.5378 and 11.1531 ppm, respectively, which are the most-shielded carbon atoms in GSL. The chemical shift of C19 bound to O1 is 58.5009 ppm.

GSL-1. The predicted ¹H chemical shifts for all hydrogen atoms on both phenyl rings, namely, H25, H26, H27, H28, H29, H30, and H31 are 7.6118, 8.4343, 8.0648, 8.3844, 7.7076, 7.7204, and 8.5002 ppm, respectively. The chemical shifts of hydrogen atoms H32, H33, H34, and H35 on C15 and C16 that are bound to N23 are 3.7322, 4.4645, 3.7208, and 4.4747 ppm, respectively. The chemical shift for hydrogen atoms H36, H37, H38, H39, H40, and H41 on C17 and C18 are 1.4565, 1.1798, 1.8907, 1.4687, 1.1891, and 1.8963 ppm, respectively. The chemical shifts of H42, H43, and H44 on C19 bonded to O1 are 4.5361, 4.0608, and 4.0499 ppm respectively. The theoretical chemical shifts, although exhibiting a downward shift relative to the experimental values, are in relatively good agreement with experimental ¹H NMR (400 MHz, CDCl₃) δ (ppm):7.93-7.96 (m, 3H), 7.28-7.29 (d, 1H, J=2.4 Hz), 7.04-7.07 (m, 1H), 6.71-6.74 (d, 2H, J=9.6 Hz), 3.89 (s, 3H), 3.46-3.52 (q, J=7.2 Hz, 4H), 1.24-1.28 (t, 6H, J=7.8 Hz).

Furthermore, the predicted ¹³C chemical shifts for both phenyl ring carbon atoms C2, C3, C4, C5, C6, C7, C9, C10, C11, C12, C13, and C14 are 159.9456, 117.3063, 125.3089, 149.0541, 138.7721, 102.0303, 143.8061, 138.1642, 114.8590, 152.3618, 116.9037, and 117.6215 ppm, respectively. The higher chemical shifts on C2, C5, C6, C9, and C12 is due to de-shielding by neighboring oxygen,

nitrogen, and sulfur atoms. The chemical shift of C8 in thiazole is 180.2112 ppm, which is the most deshielded carbon in GSL-1. The chemical shifts of shielded carbon atoms C15 and C16 bound to N23 are 42.5751 and 42.5145 ppm, respectively. In addition, the chemical shifts of C17 and C18 bound to C15 and C16 are 11.1985 and 11.1423 ppm, respectively, which are the most-shielded carbon atoms in GSL-1. The chemical shift of C19 bound to O1 is 57.4765 ppm. The theoretical chemical shifts are in good agreement with experimental ¹³C NMR (400 MHz, CDCl₃) δ (ppm): 175.32, 158.45, 151.89, 147.34, 142.45, 135.59, 127.71, 127.40, 124.53, 115.34, 111.22, 104.53, 55.71, 44.91, 12.61.

3.8 Natural Charge analysis

As the atomic charges determine many properties of molecular systems, the natural charges were computed by NBO analysis and the results are shown in Table 5-6 (atom numbering according to Fig. 1). Here, N21–24 and S25 in GSL are equivalent to N20–23 and S24 in GSL-1.

GSL. The carbon atoms on both phenyl rings are negative, except C2, C5, C9, and C12 that are bonded to electron-withdrawing nitrogen and oxygen atoms, with C2 bonded to O1 and C12 bonded to N24 being the most-positively charged carbon atoms in the molecule, whereas C3, C7, and C11, C13 are the most-negatively charged carbon atoms on the phenyl rings due to their proximity to positive C2 and C12, respectively. The rest of the carbon atoms are negative with the exception of thiazole C8, which is bonded to two electron-withdrawing nitrogen atoms and one electron-donating sulfur atom. The most-negative carbon atom in GSL is C20, which is attached to the methyl group via N21, followed by methyl C17 and C18. All oxygen and nitrogen atoms have a negative charge, with N24 being the most negative and azo N23 being the least negative nitrogen atoms in the molecule, which suggests that azo N23 is more susceptible to nucleophilic attack than azo N22. In contrast, thiazole S25 has a positive charge as it donates electrons to C6 and C8. All hydrogen atoms are positive and similarly charged with methyl H46 on C20 bonded to N21 being the most positive, whereas H44 and H45 of C19 bonded to O1 being the least positive hydrogen atoms in the molecule.

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Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
O1	-0.53035	C11	-0.31731	N21	-0.34343	H31	0.26796	H41	0.24741
C2	0.34617	C12	0.28779	N22	-0.34896	H32	0.27773	H42	0.25751
C3	-0.2687	C13	-0.2939	N23	-0.16943	H33	0.26274	H43	0.24799
C4	-0.23821	C14	-0.1734	N24	-0.37602	H34	0.25816	H44	0.22422
C5	0.12628	C15	-0.282	S25	0.50632	H35	0.26265	H45	0.22424
C6	-0.21266	C16	-0.28216	H26	0.27346	H36	0.2583	H46	0.28051
C7	-0.32642	C17	-0.71781	H27	0.27717	H37	0.24594	H47	0.2674
C8	0.29653	C18	-0.71787	H28	0.27798	H38	0.24741	H48	0.26719
C9	0.06829	C19	-0.35013	H29	0.27388	H39	0.25754		
C10	-0.14801	C20	-0.50595	H30	0.26791	H40	0.24604		

Table 5. NBO charges of GSL

GSL-1. Similar to GSL, carbon atoms on both phonyl rings are negative, except for C2, C5, C9, and C12, which are bonded to electron-withdrawing nitrogen and oxygen atoms with C2 bonded to O1, and C12 bonded to N23, being the most-positively charged carbon atoms in the molecule, whereas, C3, C7 and C11, C13 are the most negative carbon atoms on the phenyl rings due to their proximity to positively charged C2 and C12, respectively. The rest of the carbon atoms are negative, with the exception of thiazole C8, which is bonded to two electron-withdrawing nitrogen atoms and one electron-donating sulfur atom. The most-negative carbon atoms in GSL-1 are methyl C17 and C18. All oxygen and nitrogen atoms have a negative charge, with N20 being the most negative and azo N22 being the least negative in the molecule. Of the nitrogen atoms in the molecule, azo N22 has a higher susceptibility to nucleophilic attack than azo N21. Non-methylated N20 has a higher negative charge (susceptibility to electrophilic attack) in GSL-1 than in GSL. Thiazole S24 has a positive charge as it donates electrons to C6 and C8. Similar to GSL, all hydrogen atoms in GSL-1 are positive and similarly charged, with phenyl H31 being the most positive, whereas H43 and H44 of C19 bonded to O1 are the least-positive hydrogen atoms in the molecule.

Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
01	-0.53497	C11	-0.31974	N21	-0.26144	H31	0.26837	H41	0.23929
C2	0.33928	C12	0.24159	N22	-0.1887	H32	0.23983	H42	0.24311
C3	-0.29473	C13	-0.30352	N23	-0.43938	H33	0.25229	H43	0.2191
C4	-0.21685	C14	-0.1934	S24	0.37881	H34	0.23925	H44	0.21914
C5	0.09058	C15	-0.27197	H25	0.26263	H35	0.25243		
C6	-0.22012	C16	-0.27222	H26	0.26351	H36	0.25321		
C7	-0.34398	C17	-0.718	H27	0.26488	H37	0.24517		
C8	0.21511	C18	-0.71778	H28	0.26192	H38	0.23924		
C9	0.04101	C19	-0.34663	H29	0.2544	H39	0.25323		
C10	-0.17641	N20	-0.45726	H30	0.25446	H40	0.24525		

Table 6. NBO charges of GSL-1

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3.9. NBO analysis

NBO analysis was used to study the interactions between orbitals and thereby demonstrate intramolecular charge transfer, delocalization and conjugation of the electron density. The results of the NBO analysis, such as the occupation numbers, polarization coefficient values, intramolecular donor– acceptor interactions, and stabilization energies of selected bonding atoms in GSL and GSL-1 were calculated and the results are shown in Table S3-S6. The atoms are numbered according to Fig. 1, where N21–24 and S25 in GSL are equivalent to N20–23 and S24 in GSL-1, respectively. One of the phenyl rings of GSL displays a preferred quinonoid structure leaving C9 with a lone pair, and forming C12=N24 instead of C12–N24. The most stabilizing interactions in both molecules are high occupancy $\pi \rightarrow \pi^*$ transitions that move back and forth around azo N22–N23 in GSL and N21–N22 in GSL-1. High occupancy $n \rightarrow \pi^*$ and lower occupancy $n \rightarrow \sigma^*$ transitions occur from nitrogen, sulfur, and oxygen lone pairs, as well as C9 in the GSL quinonoid structure. Finally, for the low occupancy $\sigma \rightarrow \sigma^*$ transitions, sulfur-bonded atoms contribute greatly to the conjugation. In addition, the size of the polarization coefficients of the two hybrid orbitals from atom A and B demonstrates their importance in forming

bonds, where higher values indicate higher importance. The fraction of the hybrid orbital character between hybrids A and B, as well as the fraction of *p*-character, give information about the overall bond character and strength, as well as intramolecular charge transfer [26]. The oxygen atoms in both GSL and GSL-1 have the highest individual hybrid character and polarization coefficients in their C–O bonds, followed by nitrogen in C–N bonds, and carbon in C–S bonds. Both structures showed low energy hyperconjugative interactions between $\sigma \rightarrow \pi^*$.

3.10 NLO properties

NLO analysis was used to study the influence of the molecular structure on the polarizabilities and hyperpolarizabilities of the studied compounds to evaluate their suitability for optoelectronics and photonics applications. The total static dipole moment (μ), mean polarizability (α), anisotropy of polarizability ($\Delta \alpha$), and the mean first-order hyperpolarizability (β) of GSL and GSL-1 were estimated. The x,y,z components of μ , α , and β were used to extract the values of interest using the following equations [27].

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2}$$

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

$$\Delta \alpha = \frac{1}{\sqrt{2}} \sqrt{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{xz}^2)}$$

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

$$\beta = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}$$

The NLO results are shown in Table 7 and compared with urea as a reference standard. The calculated values were converted to electrostatic units (esu) from atomic units (a.u.) using a conversion

factor of 0.1482×10^{-24} for α and 8.6393×10^{-30} for β . GSL and GSL-1 showed high β values, which were 61 and 343 times higher than urea, respectively (μ =1.3732 Debye, β =0.3728×10⁻³⁰ esu) [27]. Moreover, the μ and α values of both molecules showed that GSL is preferable for linear optics applications, whereas the β values of GSL-1 show that it is favorable for applications in non-linear optics.

Parameter	GSL	GSL-1								
Dipole mon	Dipole moment (µ) Debye									
μ_x	-12.0278	-6.3476								
$\mu_{\rm y}$	0.3310	0.0279								
μ_z	39.5364	5.4400								
μ	41.3268	8.3598								
Polarizabili	ty (α) ×10 ⁻²	⁴ esu								
α_{xx}	78.9424	59.4735								
α_{xy}	-0.7080	0.3220								
α_{yy}	22.9476	20.7202								
α_{xz}	-53.2239	-34.4952								
α_{yz}	1.5576	0.3379								
α _{zz}	144.5349	113.4435								
α	82.1416	64.5457								
Δα	140.0635	100.3818								
Hyperpolar	izability (β) ×10 ⁻³⁰								
esu										
β_{xxx}	14.6161	-9.8200								
β_{xxy}	-1.1254	0.0642								
β_{xyy}	0.3219	0.7667								
β_{yyy}	-0.0179	-0.0057								
β_{xxz}	3.0623	27.6162								
β_{xyz}	0.3886	-0.1545								
β_{yyz}	-0.0998	-0.2888								
β_{xzz}	-22.9894	-54.3163								
β_{yzz}	1.4952	0.2476								
β_{zzz}	18.4321	83.8290								
β_x	-8.0514	-63.3696								
β_y	0.3519	0.3061								
β_z	21.3946	111.1564								
β	22.8621	127.9514								

Table 7. NLO parameters of GSL and GSL-1

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CONCLUSION

The calculated parameters of GSL and GSL-1 revealed differences in their electronic properties, MEP maps, NBO parameters and NLO properties. The preferred quinonoid structure of one of the phenyl rings of GSL explains the red-shift observed in the UV-Vis spectrum. Both molecules display charge transfer capabilities through light absorption in the visible range. However, the additional methyl group in GSL generates a charged molecule that prevents use of a protic solvent, which limits the extent of a realistic comparison of the two structures. The electronic properties, including the HOMO–LUMO gap, are affected by the choice of solvent, as well as the NBOs, and MEP maps. The NLO values were enhanced in the presence of water, especially the hyperpolarizability values; however, benchmarking gasphase calculations suggest similar favorable trends compared to the values in solvent with respect to the NLO activity of GSL and GSL-1. Overall, the results presented here provide a foundation for further studies using GSL and GSI-1 for optoelectronic and photonic applications.

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References

- [1] J.P. Soni, K.S. Chemitikanti, S.V. Joshi, N. Shankaraiah, The microwave-assisted syntheses and applications of non-fused single-nitrogen-containing heterocycles, Org. Biomol. Chem. 18(48) (2020) 9737–9761. doi: 10.1039/d0ob01779e.
- [2] G. Verma, A. Marella, M. Shaquiquzzaman, M. Akhtar, M.R. Ali, M.M. Alam, A review exploring biological activities of hydrazones, J. Pharm. Bioallied Sci. 6(2) (2014) 69–80. doi: 10.4103/0975-7406.129170.
- [3] P. Mondal, R. Kumar, R. Gogoi, Azomethine based nano–Chemicals: Development, in vitro and in vivo fungicidal evaluation against Sclerotium rolfsii, Rhizoctonia bataticola and Rhizoctonia solani, Bioorg. Chem. 70 (2017) 153–162. doi: 10.1016/j.bioorg.2016.12.006.
- [4] M. Yadav, S. Sharma, J. Devi, Designing, spectroscopic characterization, biological screening and antioxidant activity of mononuclear transition metal complexes of bidentate Schiff base hydrazones, J. Chem. Sci. 133(1) (2021). doi: 10.1007/s12039-020-01854-6.
- [5] V. Manzoni, L. Modesto-Costa, J. Del Nero, T. Andrade-Filho, R. Gester. Strong enhancement of NLO response of methyl orange dyes through solvent effects: A sequential Monte Carlo/DFT investigation. Opt. Mater. 94 (2019), 152-159. doi: 10.1016/j.optmat.2019.05.018
- [6] A. Bogdanov, A. Vorobiev. Photo-orientation of azobenzene-containing liquid-crystalline materials by means of domain structure rearrangement. J. Phys. Chem. B, 117(44) (2013) 13936-13945. doi: 10.1021/jp4080509

- [7] H. Etesami, M. Mansouri, A. Habibi, F. Jahantigh. Synthesis and investigation of double alternating azo group in novel para-azo dyes containing nitro anchoring group for solar cell application. J. Mol. Struct. 1203 (2020) 127432. doi: 10.1016/j.molstruc.2019.127432
- [8] ADF, SCM, 2020, http://www.scm.com. Theoretical Chemistry, Vrije Universiteit Amsterdam, The Netherlands.
- [9] G. te Velde, F.M. Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. van Gisbergen,
 J.G. Snijders, T. Ziegler, Chemistry with ADF, J. Comp. Chem. 22(9) (2001) 931–967.
 https://doi.org/10.1002/jcc.1056.
- [10] L. Fan, T. Ziegler, Application of density functional theory to infrared absorption intensity calculations on main group molecules, J. Chem. Phys. 96(12) (1992) 9005–9012. https://doi.org/10.1063/1.462258.
- [11] E. van Lenthe, E.J. Baerends, Optimized Slater-type basis sets for the elements
 1–118, J. Comp. Chem. 24(9) (2003) 1142–1156. https://doi.org/10.1002/jcc.10255.
- C.C. Pye, T. Ziegler, An implementation of the conductor-like screening model of solvation within the Amsterdam density functional package, Theor. Chem. Acc. Theor. Comput. Model. (Theor. Chim. Acta) 101(6) (1999) 396–408. https://doi.org/10.1007/s002140050457.
- [13] E. van Lenthe, E.J. Baerends, J.G. Snijders, Relativistic regular two-component Hamiltonians, J. Chem. Phys. 99(6) (1993) 4597–4610. https://doi.org/10.1063/1.466059.
- [14] E. van Lenthe, E.J. Baerends, J.G. Snijders, Relativistic total energy using regular approximations, J. Chem. Phys. 101(11) (1994) 9783–9792.
 https://doi.org/10.1063/1.467943.

- [15] E. van Lenthe, A. Ehlers, E. Baerends, Geometry optimizations in the zero order regular approximation for relativistic effects, J. Chem. Phys. 110(18) (1999) 8943–8953.
 https://doi.org/10.1063/1.478813.
- [16] S.J.A. van Gisbergen, J.G. Snijders, E.J. Baerends, Implementation of timedependent density functional response equations, Comput. Phys. Commun. 118(2–3) (1999) 119–138. https://doi.org/10.1016/S0010-4655(99)00187-3.
- [17] J. Autschbach, T. Ziegler, Nuclear spin–spin coupling constants from regular approximate relativistic density functional calculations. I. Formalism and scalar relativistic results for heavy metal compounds, J. Chem. Phys. 113(3) (2000) 936–947. https://doi.org/10.1063/1.481874.
- [18] F. Wang, T. Ziegler, A simplified relativistic time-dependent density-functional theory formalism for the calculations of excitation energies including spin-orbit coupling effect, J. Chem. Phys. 123(15) (2005) 154102. https://doi.org/10.1063/1.2061187.
- [19] G. Schreckenbach, T. Ziegler, Calculation of NMR shielding tensors using gauge-including atomic orbitals and modern density functional theory, J. Phys. Chem. 99(2) (1995) 606–611. https://doi.org/10.1021/j100002a024.
- [20] NBO, 7 0. E.D. Glendening, J, K. Badenhoop, A. E. Reed, J. Eng. Carpenter, J. A. Bohmann, C. M. P. Karafiloglou, Morales, C. R. Landis, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison (2018).
- M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R.
 Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato,
 A. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V.
 Ortiz, A.F. Izmaylov, J.L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F.

Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J.
Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J.
Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K.
Throssell, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E.
Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K.
Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam,
M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas,
J.B. Foresman, D.J. Fox, Gaussian, Inc., Wallingford CT, Gaussian 09, Revision D.01 (2016).

- [22] M. Sheikhi, S. Shahab, R. Alnajjar, M. Ahmadianarog, Adsorption properties of the new anti-cancer drug alectinib on CNT(6,6-6) Nanotube: Geometry Optimization, Molecular Structure, Spectroscopic (NMR, UV/Vis, Excited State), FMO, MEP and HOMO–LUMO Investigations, J. Clust. Sci. 30(1) (2019). https://doi.org/10.1007/s10876-018-1460-9.
- [23] S. Shahab, M. Sheikhi, L. Filippovich, Z. Ihnatovich, E. Koroleva, M. Drachilovskaya et al., Spectroscopic (FT-IR, excited states, UV/vis, polarization) properties, synthesis and quantum chemical studies of new azomethine derivatives, Dyes Pigments 170 (2019). https://doi.org/10.1016/j.dyepig.2019.107647, 107647.
- S. Shahab, H.A. Almodarresiyeh, L. Filippovich, F.H. Hajikolaee, R. Kumar, M. Darroudi, M. Mashayekhi, Geometry optimization and excited state properties of the new symmetric (E)-stilbene derivative for application in thermostable polarizing PVA-films: A combined experimental and DFT approach, J. Mol. Struct. 1119 (2016) 423–430. https://doi.org/10.1016/j.molstruc.2016.04.092.

- [25] S. Siyamak Shahab, M. Sheikhi, L. Filippovich, E. Dikusar, M. Darroudi, S. Kaviani et al., Optimization, spectroscopic (excited states, UV/vis, polarization) studies, FMO, ELF, LOL, QTAIM, NBO analysis and electronic properties of two new azomethine derivatives: A theoretical and experimental investigations, Russ. J. Phys. Chem. A 94(9) (2020) 1848–1865. https://doi.org/10.1134/S0036024420090241.
- [26] S. Shahab, M. Sheikhi, E. Kvasyuk, A.G. Sysa, R. Alnajjar, A. Strogova et al.,
 Geometry optimization, UV/vis, NBO, HOMO and LUMO, excited state and antioxidant
 evaluation of pyrimidine derivatives, Lett. Org. Chem. 17 (2020).
 https://doi.org/10.2174/1570178617999200812133402.
- [27] J. Prashanth, G. Ramesh, J.L. Naik, J.K. Ojha, B.V. Reddy, G.R. Rao, Molecular Structure, vibrational analysis and first order hyperpolarizability of 4-Methyl-3– Nitrobenzoic acid using density functional theory, Opt. Photonics J. 05(3) (2015) 91–107. doi: 10.4236/opj.2015.53008.

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Graphical Abstract

