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Spectroscopic behavior, FMO, NLO and substitution effect of 2-(1H-Benzo [*d*]imidazole-2-ylthio)-N-o-substituted-acetamides: Experimental and theoretical approach



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ABSTRACT

The benzimidazole-based derivatives **2a-c** were designed and synthesized via C–N coupling reaction and experimentally characterized by infrared spectroscopy (FT-IR), nuclear magnetic resonance (¹H NMR) spectroscopy and mass spectrometry (MS). The observed and calculated FT-IR frequencies correspond to C=O stretching of amide group are depicted at 1657, 1672 and 1682, 1689 and 1699, 1682 for **2a**, **2b** and **2c** respectively and are in good agreement. The synthesized compounds **2a-c** exhibit non-linear optical response with the first hyperpolarizability (β_0) at 783, 1550 and 694 au, respectively. Due to the presence of electron withdrawing $-NO_2$ on the primary amine of **2b**, the β_0 value is estimated at 1550 au, which reduces the energy barrier hence increasing the β_0 value, with maximum UV-vis absorption at 224 nm with TD-DFT method. The opposite behavior is demonstrated by the electron donor $-OCH_3$ substituent. This study of NLO responses would be beneficial to the development of high-performance NLO materials.

1. Introduction

Since the past few decades, the organic nonlinear optical (NLO) materials gain the attention of experimental and theoretical investigators because of their potential applications in modern-day devices [1,2]. There are several NLO materials have been designed, synthesized and characterized both theoretically and experimentally. Among these studied NLO compounds, the organic materials have certain advantages over other inorganic or hybrid materials, such as vast structural diversity, a broad range of optical susceptibilities and higher NLO thresholds. The modulation of molecular hyperpolarizabilities is the fundamental property to characterize any class of NLO materials [3]. There are several structural modification techniques used to modulate the NLO response such as donor- π -acceptor configurations, metal doping, bond length alteration, functional group replacements and so forth [4–10].

The heterocyclic compounds especially 2-substituted benzimidazoles derivatives exhibit a broad range of biological, pharmacological and agricultural activities such as antibacterial, antiviral, anti-ulcer, anti-inflammatory, anti-cancer, anti-HIV and anti-corrosion activities [11,12]. Organic compounds with both nitrogen and sulfur reflect better activity against several biological diseases. Benzimidazole, being an important constituent of several synthetic drugs, is also the major component of Vitamin B_{12} [13]. The structural alteration and enhancement of the existing abilities of the bioactive species are highly challenging in material chemistry. To achieve potential NLO response and efficient bioactivity of benzimidazole derivatives, exploitation can be carried out via functional group substitution. Recently, various such materials were extensively explored for their potential NLO applications as well as biological applications. Muhammad et al., successfully tuned the hyperpolarizabilities of benzimidazole derivatives by proton abstraction [14]. Yu et al., also synthesized the hybrid benzimidazole derivatives with efficient NLO responses [15]. Yadav et. al., demonstrated the synthesis and biological evaluation of 2-(1-benzoyl-1Hbenzo[d]imidazole-2-ylthio)-N-substituted acetamides as antimicrobial, antitubercular and anticancer agents [16]. Similarly, Mao and coworkers also reported some bioactive derivatives with -COO at ortho position as protein methyltransferase 5 (PRMT5) inhibitors [17]. Mavrova et. al., also reported the biological activities of 5(6)-(un)substituted-1H-benzimidazol-2-ylthioacetylpiperazine derivatives [18]. However, there is no sufficient literature available which highlight both theoretical and experimental studies of these type of donor-acceptor benzimidazole-based derivatives. Whereas, there are recent analogues studies have been reported by Muhammad and fellow collaborators on chalcone, glycinium picrate, thiazole, and benzothiazole derivatives [8,19,20]. The combination of both theoretical and experimental

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techniques provides a better understanding of compound behavior at the molecular level. Therefore, in order to determine the structural as well as spectroscopic abilities of benzimidazole derivatives, this field attracts several theoretical and model chemists [17,18,21,22].

From the literature review, there is no such work has been found so far on these type of molecules. Therefore, to enhance the applications of these types of benzimidazole derivatives and obtain detailed structural, spectroscopic as well as nonlinear optical properties of these bioactive species, we combined the experimental and theoretical methods. Herein, we report the synthesis, characterization and optical properties of 2-(1H-Benzo[*d*]imidazole-2-ylthio)-N-substituted acetamides, primarily comparing their experimental as well as theoretical IR and ¹H NMR spectroscopic studies and theoretically estimated FMOs, and nonlinear optical properties.

The 2-(1H-Benzo[d]imidazole-2-ylthio)-N-substituted acetamides **2a-c** have been obtained upon hydrolysis of thiazolo[3,2-*a*]benzimidazol-3(2H)-ones **1** with an ortho-substituted primary amine in ethanol under reflux conditions. The ortho-substituted primary amine, with electron-rich $-CH_3$, $-OCH_3$ and electron deficient $-NO_2$ group, was selected to predict the change in chemical behavior and optical properties of synthesized compounds. In this work, theoretical studies have been performed on synthesized compounds to manipulate the effect of electron donor/acceptor substituents on electronic structures, hence, the detailed analysis of the geometric structures and appropriate nonlinear optical properties has been carried out and reported.

2. Methodology

2.1. Instruments

All reagents and solvents were used as obtained from the suppliers, or recrystallized or redistilled as necessary. Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. IR spectra (KBr disks) were run on Shimadzu (Japan) Prestige-21 FT-IR spectrometer. ¹H NMR spectra were recorded in C₂D₆SO on Bruker (Rhenistetten-Forchheim, Germany) AM 300 spectrometer operating at 300 MHz, using tetramethylsilane (TMS) as an internal standard. Proton chemical shifts are reported in δ (ppm) whereas coupling constants in Hz. Electron impact (EI) mass spectra were recorded on JEOL MS Route mass spectrometer. Thin layer chromatography using glass plates coated with Silica gel 60 GF₂₅₄ (E.Merck) was carried out to monitor the progress of the reactions and purity of the products. The spots were visualized under The UV-light at 254 and 366 nm and iodine vapors were used to visualize the spots The structural optimization, Nonlinear optical properties and UV-vis absorption estimations for these molecules were performed at B3LYP/6-31G(d) and CAM-B3LYP/6-31 + G(d) level, respectively, using the Gaussian 09 program package [14,23].

2.2. Synthesis

The synthetic route to achieve target compounds **2a-c** is shown in Scheme 1 and structures of synthesized molecules are presented in Fig. 1. The syntheses of three 2-(1H-Benzo[*d*]imidazole-2-ylthio)-N-substituted acetamides **2a-c** are carried out via hydrolysis of thiazolo [3,2-*a*]benzimidazole-3(2H)-one **1** in ethanol with an o-substituted primary amine, with a yield of 46%, 47%, and 38%, respectively. The final products are characterized by standard spectroscopic techniques. To a hot stirred solution of thiazolo[3,2-*a*]benzimidazole-3(2H)-one (1) (0.001 mol) in ethanol (5 ml) containing a few drops of acetic acid was added an appropriate amine (0.001 mol) dissolved in ethanol (5 ml). The resultant mixture was then refluxed for 2–6 h and the solid formed during heating under reflux was filtered hot. The desired products were obtained by thorough washing with hot ethanol in the pure form. Hence, low yields of synthesized compounds could be increased via column chromatography and further purification.

2-(1H-Benzo [*d*] imidazole-2-ylthio)-N-*o*-tolylacetamide (2a). Melting point: 165–167 °C; Yield: 47%; IR (KBr, cm⁻¹): 3288, 3045, (NH stretching), 1657 (C=O stretching); ¹H-NMR (DMSO- d_6 , δ ppm): 2.19 (s, 3H, CH₃), 4.23 (s, 2H, CH₂), 7.04 (m, 4H, benzimidazole), 7.38 (m, 4H, phenyl ring), 9.85 (s, 1H, imidazole NH), 12.69 (s, 1H, aryl NH); **MS** (70 eV), *m/z* (rel. int.) (%): 297 (M+, 16), 223 (4), 191 (27), 164 (100), 150 (16), 131 (53), 119 (16), 107 (45), 83 (21), 65 (5), 51 (3).

2-(1H-Benzo [d] imidazole-2-ylthio)-N-(2-nitrophenyl)acet-

amide (2b). Melting point: 210–212 °C; Yield 46%; **IR** (KBr, cm⁻¹): 3171, 3140, (NH stretching), 1672 (C=O); ¹H-NMR (DMSO- d_{6} , δ ppm): 4.31 (s, 2H, CH₂), 7.36 (m, 4H, benzimidazole), 7.75 (m, 4H, phenyl ring), 10.97 (s, 1H, imidazole NH), 12.66 (s, 1H, aryl NH); **MS** (70 eV), m/z (rel. int.) (%): 328 (M+, 18), 191 (13), 164 (100), 150 (14), 131 (44), 118 (14), 92 (6), 63 (4).

2-(1H-Benzo [*d*] imidazole-2-ylthio)-N-(2-methoxyphenyl)acetamide (2c). Melting Point: 165–167 °C; Yield: 38%; **IR** (KBr, cm⁻¹): 3182, 3045, (NH stretching), 1682 (C=O); ¹H-NMR (DMSO- d_6 , δ ppm): 3.67 (s, 3H, OCH₃), 4.20 (s, 2H, CH₂), 6.98 (m, 4H, phenyl ring), 7.15 (m, 4H, benzimidazole), 9.93 (s, 1H, imidazole NH), 12.71 (s, 1H, aryl NH); **MS** (70 eV), *m*/*z* (rel. int.) (%): 314 (M+, 8), 282 (5), 191 (59), 164 (100), 150 (25), 131 (97), 123 (100), 108 (42), 92 (19), 80 (17), 65 (21), 52 (12).

2.3. Quantum chemical details

In order to achieve profound insight into the distribution of electrons and geometrical configuration of the studied compounds 2a-c, DFT calculations were carried out using Gaussian 09 package. Firstly, geometric estimations and vibrational frequencies were at B3LYP and PBE0 with 6-31G(d) basis set and the obtained results are summarized in Table S1 & Table S2 respectively. The optimized geometric structure with atom labeling for 2a is expressed in Fig. 2. To make sure the optimized geometries are real minima, all frequency calculations were cross-checked and these are found to be positive values, as no imaginary frequencies present on the related potential energy surfaces. Hence, B3LYP optimized geometry is selected for further estimations because the results obtained with this method are more consistent with some reported benzimidazole derivatives [14,24,25]. From the ground state optimized geometries, the vibrational frequencies and ¹H NMR chemical shifts of the studied molecules were estimated in the ethanol as a solvent. To explore the origin of second-order NLO response, TD-DFT calculations were performed to estimate the nature of the excited state with CAM-B3LYP/6-31 + G* method [5,26]. Moreover, to determine the effect of substitution on nonlinear optical properties, the static first hyperpolarizability β_o was obtained by the finite field (FF) method at CAM-B3LYP/6-31 + G* level. The FF approach was developed by Kurtz et al., has been widely used to estimate the first hyperpolarizabilities because it provides a reasonable agreement with experimental NLO responses. In this FF method, a static electric field (F) is applied and the energy (E) of the molecule is expressed by the following equation:

$$E = E^{(0)} - \mu_1 F_1 - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \frac{1}{24} \gamma_{ijkl} F_i F_j F_k F_l - \dots$$
(1)

Here, $E^{(0)}$ represents the total energy of molecule in the absence of an electric field, μ is the vector component of the dipole moment, α is the linear polarizability, β and γ are the second and third-order polarizabilities, respectively, while *x*, *y* and *z* label the *i*, *j*, *k* components, respectively. It can be seen from eq. (1) that differentiating *E* with respect to *F* obtains the μ , α , β , and γ values. In this investigation, we have calculated the electronic dipole moment, molecular polarizability, and molecular first hyperpolarizability. For a molecule, its dipole moment (μ) is defined as follows:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2) \tag{2}$$



Scheme 1. The synthetic pathway of the studied molecules 2a-c.

The average polarizability (α_0) can be calculated by the following equation:

$$\alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{3}$$

Similarly, the magnitude of the total static first hyperpolarizability can be calculated using the following equations:

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{\frac{1}{2}}$$
(4)

in which

$$\begin{split} \beta_{x} &= \beta_{xxx} + \beta_{xyy} + \beta_{xzz}, \\ \beta_{y} &= \beta_{yyy} + \beta_{xxy} + \beta_{yzz}, \\ \beta_{z} &= \beta_{zzz} + \beta_{xxz} + \beta_{yyz}, \end{split}$$

.

while the static first hyperpolarizability (β_0) is also calculated using the following equation:

$$\beta_0 = \frac{3}{5}(\beta_{tot}) \tag{5}$$



Fig. 2. The optimized structure of studied molecule 2a with atom numbering.

The second-order polarizability (β), that is a third rank tensor and can be described by $3 \times 3 \times 3$ matrix. According to Kleinman symmetry ($\beta_{xyy} = \beta_{yxy} = \beta_{yyx}$, $\beta_{yyz} = \beta_{yzy} = \beta_{zyy}$, ...likewise other permutations also take the same value), the 27 component of the 3D matrix can be reduced to ten components. All reported β values are expressed in atomic units [1 a.u. of $\beta = 3.62 \times 10^{-42} \text{ m}^4 \text{ V}^{-1} = 3.2063 \times 10^{-53} \text{ C}^3 \text{ m}^3 \text{ J}^{-2} = 8.641 \times 10^{-33} \text{ esu}$] within the T convention.



Fig. 1. Chemical structures of the synthesized compounds 2a-c.

3. Results and discussions

3.1. Geometry optimization

The geometry optimization of all studied molecules is summarized in Table S3. As there is no crystallographic data of this molecule has been reported, different synthesized compounds of thiazolo-benzimidazole and its derivatives were considered to evaluate the optimized geometry of the synthesized molecules. As the -OCH₃ and -NO₂ substituents are present on the far ends, the structural parameters of the optimized geometries are moderately affected. Table S3 revealed that C7–N12 is 1.31 Å, and C7–N13 is 1.37 Å resembling C=N (1.306 Å) and C-N (1.364 Å), the bond of benzimidazole [27] indicates that C7-N12 is as possible as double bond and C7-N13 is more likely a single bond [27]. Whereas, N18-C24 is the longest C-N bond exists in the studied molecules with a bond length of 1.41 Å, evidencing that N18-C24 is a free single bond of o-toluidine [28]. The length of the C23-N32 bond is 1.45 Å, hinting that it is a single bond of -NO₂ substitution at the ortho position of o-toluidine. The bond lengths of (Ph)C–N in this molecule are ranging between 1.3779 and 1.3823 Å, revealing their single character with some p ingredients. As reported earlier, the lengths of (Ph)C-N bonds are 1.372, 1.395 Å and 1.379, 1.388 Å for benzimidazole and 5-amino-1-methyl-1H-benzimidazole [29,30], respectively. The bond distance of C7–S15, S15–C16 are about 1.76 Å and 1.83 Å respectively, which deviates from normal C-S bond length 1.80 Å [31], may be the cause of pulling interactions of the benzimidazole moiety on C7. The dihedral angles of benzimidazole and o-toluidine parts are almost equal to 180 or 0. On the other hand, the bond lengths of C23C33 1.51, C23N32 1.45 and C23O33 1.36 correspond to C-CH₃, C-NO₂, and C-OCH₃ of different substitutions. Whereas, C24C23C33 121.6, C24C23N32 123.1 and C24C23O33 114.7 correspond to bond angles of these substituted groups. These differences in geometric structures are the source to produce different NLO responses.

3.2. Vibrational assignments

The experimental and calculated IR spectra are presented in Fig. 3. In general, the DFT methods provide excellent vibrational wavenumbers for organic molecules. For comparison with experimental results, a proper scaling factor is required to compensate the overestimation of the vibrational frequencies obtained with quantum calculations (0.9613 for B3LYP method [29]). The recorded and calculated vibrational frequencies are in good consistency, supports the reliability of the used method.

The vibrations C–H and C–C of aromatic rings provide obvious characteristics. The C–H stretching vibrations of phenyl rings usually observed at 3030-3100 cm⁻¹. The bending vibrations of C–H often absorb in the range of 1000-1300 cm⁻¹, whereas, the C–H vibrations around 650-900 cm⁻¹ correspond to out-of-plane bending vibrations.

Table 1

The experimental and computed ${}^{1}H$ NMR chemical shifts of all synthesized compounds **2a-c**.

2a			2b		2c	
Atom	Exp (ppm)	Calc ^a (ppm)	Exp (ppm)	Calc ^a (ppm)	Exp (ppm)	Calc ^a (ppm)
8-H 9-H 10-H 11-H 14-H 19-H 26-H 28-H 30-H 31-H 32-H 34-H 35-H	7.04 7.04 7.04 9.85 7.33 7.38 7.38 7.38 4.23 4.23 4.23 12.69 2.19	7.06 7.06 7.06 9.68 7.31 7.32 7.32 4.28 4.26 10.54 2.23 2.23	7.36 7.36 7.36 7.75 12.66 7.75 7.75 7.75 4.31 4.31	7.34 7.35 7.34 8.09 10.71 7.78 7.77 7.77 4.34 4.35	7.15 7.15 7.15 9.93 7.43 6.98 6.98 6.98 4.20 4.20 12.71 3.67	7.18 7.18 7.18 7.18 9.68 7.38 7.07 7.02 7.11 4.24 4.24 10.46 3.62
36-Н 37-Н	2.17	2.20	10.97	5.55	3.67 3.67 3.67	3.62 3.63

^a Calculated with B3LYP/6-31G(d) method.

The C–C stretching vibrations of the phenyl rings often observed around 1450, 1500, 1580 and 1600 cm⁻¹. The C–C and C–H stretching vibrations of the phenyl ring of benzimidazole are reported between the range of 1588–1620 cm⁻¹ and 2096-3062 cm⁻¹, respectively, and the vibrations under 1000 cm⁻¹ correspond to C–H out-of-plane bending vibrations of the phenyl ring of benzimidazole [31–33]. The peaks around 3288 cm⁻¹, 3045 cm⁻¹ assigned to stretching vibrations of benzimidazole hydrogen and NH hydrogen of respective amine respectively, whereas peak around 1657 cm⁻¹ corresponds to intense C= O stretching.

3.3. Nuclear magnetic resonance

The values of NMR collected from the recorded spectra are expressed as follows:

¹**H-NMR** (DMSO- d_6 , δ ppm): 4.31 (s, 2H, CH₂), 7.36 (m, 4H, benzimidazole), 7.75 (m, 4H, phenyl ring), 10.97 (s, 1H, imidazole NH), 12.66 (s, 1H, aryl NH) for studied molecule **2b**.

The observed and estimated chemical shift values are in concert with peak assignments and summarized in Table 1. The ¹H NMR spectra of these systems were recorded using DMSO- d_6 as a solvent with TMS as an internal standard. The quantum chemical estimations have been performed with the B3LYP/6-31G(d) method through gauge-including atomic orbital (GIAO) approach. The Obtained chemical shift values are converted to the TMS scale by subtracting the calculated absolute chemical shielding of TMS ($\delta = \Sigma_0 - \Sigma$), where δ is the chemical shift, Σ



Fig. 3. Experimental and calculated FT-IR spectra of synthesized compounds (a) 2a, (b) 2b and (c) 2c.



Fig. 4. Correlation graphs of observed and estimated chemical shifts of synthesized compounds (a) 2a, (b) 2b and (c) 2c.

is the absolute shielding and Σ_o is the absolute shielding of TMS, whose value is 31.64 at B3LYP/6-311 $\,+\,$ G (2d,p) level.

For a fair comparison with observed values, the correlation graphs are presented in Fig. 4, whereas, the correlation coefficient 0.9106 is also considered. A good agreement has been found between the estimated and recorded proton chemical shifts values.

3.4. Dipole moment, first hyperpolarizability and frontier molecular orbital analysis

The fundamental electronic responses of the studied compounds are ground state dipole moments and the first hyperpolarizability values are summarized in Table 2 and Table 3, respectively. Usually, the direction of the ground state dipole moment is from negative to positive part of the molecule. The strong electron withdrawing moiety $(-NO_2)$ substituted at the ortho position of the primary amine enhances the charge separation within the molecule, resulting in the highest ground state dipole moment for **2b**. Alternatively, the $-CH_3$ and $-OCH_3$ substitution on the same part of the compounds **2a** and **2c**, respectively, resulting in less charge separation and lower ground state dipole moments. The main charge transfer axis in all synthesized compounds is the y-axis, becoming the major component of dipole moment. This supports the fact that the ground state dipole moment can be tuned by swapping the donor/acceptor substituents.

The large nonlinear optical response as a structure-property relationship can be best estimated by quantum chemical calculations [34–37]. The nonlinear optical susceptibilities of the all synthesized compounds are characterized by the first hyperpolarizability. In this work, the static (β_0) first hyperpolarizabilities have been calculated according to eq. (5) and presented in Table 3.The graphical representation of static first hyperpolarizability (β_0) estimated at CAM-B3LYP and PBE0 is given in Fig. 5. From Table 3, it can be depicted that the **2c** has the smallest amplitude of β_0 694 a.u., which reflects the electron donating behavior of $-OCH_3$ substitution resulting in less charge separation supports the lowest β_0 values for this system.

Whereas, the replacement of this functional group with $-CH_3$ and $-NO_2$, the electron donating/withdrawing effect of these functional groups show interesting changes in these derivatives. The $-NO_2$ substitution of **2b** significantly enhances the charge separation because of

Table 2

The calculated ground state dipole moment (μ_{tot}) of all synthesized compounds $\mbox{2a-c}.$

Components	2a	2b	2c
μ_x	-0.866	1.041	0.958
μ_y	2.581	- 4.249	3.664
μ_z	-0.001	- 0.196	-0.089
μ_{tot} (Debye)	2.723	4.379	3.788

Table 3

The calculated first hyperpolarizabilities (β_0) along with their individual components for all synthesized compounds obtained with CAM-B3LYP/6-31 + G(d) method.

β components	2a	2b	2c
β _{xxx}	1084	- 539	-1027
β _{xxy}	0	476	134
β _{xyy}	- 39	- 539	-208
β _{γγγ}	0	1963	-250
β_{xxz}	-145	2	3
β_{xyz}	0	7	5
Byyz	- 35	-10	-1
β_{xzz}	167	-7	91
$\beta_{\gamma z z}$	0	- 94	-53
β_{zzz}	- 306	-1	-3
β_x	727	-651	-687
β_{γ}	0	1407	-101
β_z	- 292	-6	-1
β_0	783	1550	694



Fig. 5. Relationship between the first hyperpolarizability and –CH₃, –NO₂ and –OCH₃ substituents with two density functional methods.

its electron accepting ability, hence, increasing the β_{o} amplitude to 1550 a.u. which is about twice than that of compound **2c**. While in **2a**, the substitution of $-CH_3$ functional group moderately affects the β_{o} value up to 783 a.u. This is due to the smaller electron donating ability of $-CH_3$ as compared to $-OCH_3$, still causing the intermolecular charge transfer and modulating the first hyperpolarizability value in this system. The values of first hyperpolarizabilities of **2b** is significantly higher than the standard NLO molecule *p*-nitroaniline (PNA = 908 a.u. at CAM-B3LYP/6-31 + G* level of theory), whereas, β_0 amplitude of



Fig. 6. HOMO-LUMO representation of the studied molecule 2b at CAM-B3LYP/6-31 + G (d) level.

$$v(r) = \sum_{a} \frac{z_{a}}{r - R_{a}} - \int \frac{\rho(r')}{r - r'} dr'$$
(6)

2a, 2b and 2c is 57, 113 and 58 times larger than urea (14 a.u. at CAM-B3LYP/6-31 + G* level of theory), which is also used in literature as standard NLO molecule. The higher NLO response of **2b** can be explained by the strong electron-withdrawing effect of $-NO_2$ which may be reducing the energy barrier with substantial frontier orbital overlaps as explained in the next section. Conclusively, it can be stated that the NLO responses of the organic systems can be modulated by the substituting the electron donating/withdrawing functional groups in these kinds of organic molecules.

Frontier molecular orbitals (FMOs) provide significant information to explain the spectral behavior and fluorescence abilities. Moreover, the kinetic stability, chemical reactivity and optical polarizability of any molecule can be described from the HOMO-LUMO energy gap. The HOMO-LUMO energy gap for compound 2b is found to be 3.04eV supports its higher stability and optical response, Fig. 6. The intermolecular charge transfer can be characterized by the excitation of an electron from the occupied orbital (HOMO-i) to unoccupied orbital (LUMO + i) where i = 0,1,2 ..., and can be depicted from the graphical representation of the HOMO(s) and LUMO(s) orbitals for all studied molecules presented in Table S4. When comparing with the LUMO, frontier molecular orbital diagrams of studied systems revealed that the electron density of the respective HOMO is more extended at the electron-rich benzimidazole part which is located farther away from the respective phenyl-amine except for 2c which is due to electron donating ability of -OCH₃ substituent at the primary amine.

In order to achieve further insight into the dipole moment, we have also performed the molecular electrostatic potential (MEP) analysis, which has been carried out by the molecular charge density using the following equation:where Z_a represents a charge of the α -th nucleus at position R_a . The origin of the dipole moment can be obtained by distant charge separation. MEP represents the electrophilicity or nucleophilicity of the molecule. MEP maps are presented in Fig. 7. For example, the red surface contains a maximum negative charge and is the preferred site for electrophilic attack. While the blue color represents the maximum positive region and is preferred site for nucleophilic attack. It can



Fig. 7. The total electron density mapped with the MEP surface for 2a, 2b, and 2c (Red regions designate negative charge, while blue regions stand for a positive charge). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

be depicted form Fig. 7, that the molecular charges of compound **2a** and **2c** are uniforms, with negative potential is on carbonyl group and negative charge is on the nitrogen atom of benzimidazole part. Moreover, the MEP of 2b represents a more charge separation because of negative charge is seen on the carbonyl group as well as $-NO_2$ functional group whereas positive charge density on the nitrogen atom of benzimidazole moiety. The MEP plots are consistent with the above mentioned electronic dipole moments and first hyperpolarizabilities. The $-NO_2$ substitution of 2b compound act as an electron acceptor by withdrawing the electron density form the benzimidazole part towards primary amine as seen in the potential map. These MEP results are also in line with some similar reported systems [38–40].

3.5. Comparative analysis of first hyperpolarizability

As mentioned earlier there has been no literature available combining both experimental and theoretical studies of these type of molecules. From the literature review, we have sorted out some organic systems bearing similar terminal functional groups to make a comparison with our studied systems. It is worth mentioning that all the β_0 values reproduced in Table 4 are theoretically reported earlier using almost the same methodologies as in present work. From this comparative analysis, it can be seen that the first hyperpolarizability values (β_0)of our synthesized systems are significantly higher than other reported systems bearing the same terminal functional groups [19,41–44]. Especially the β_0 value of **2b** is roughly 85–185 folds larger than other systems represented in Table 4. This analysis support that our studied compounds might be used as potential NLO materials.

3.6. TD-DFT studies

In order to explain the second-order NLO responses, TD-DFT method was used to simulate the UV–visible absorption spectra of all studied systems and presented in Table 5. The absorption spectra are calculated using the TD-DFT method on the ground state geometries at CAM-B3LYP/6-31 + G* theory level and the estimated absorption spectra of the studied molecules is shown in Fig. 8. The substitution of electron donor/acceptor functional groups in these compounds is obvious from the change in absorption wavelengths and oscillator strengths. The electron donor functional groups decrease the absorption wavelengths to 202 nm and 203 nm for $-CH_3$ (2a) and $-OCH_3$ (2c) substituted systems, respectively, whereas the absorption at 224 nm corresponds to electron withdrawing $-NO_2$ (2b) substituted system.

As reported in the literature, a strong bathochromic shift leads to the enhanced first hyperpolarizability, from Fig. 8, it is obvious that synthesized compound **2b** has an obvious red-shift, which supports its higher dipole moment and second-order NLO response.

Table 4

Comparison of theoretically estimated β_0 amplitudes of some recently reported compounds bearing similar terminal functional groups.

Compound	β_0 (a.u.)	Methodology	Ref./Year
2-(1H-Benzo[d]imidazole-2-ylthio)-N-o-tolylacetamide 2-(1H-Benzo[d]imidazole-2-ylthio)-N-(2-nitrophenyl)acetamide 2-(1H-Benzo[d]imidazole-2-ylthio)-N-(2-methoxyphenyl)acetamide (2E)-1-(2,5-dimethylthiophen-3-yl)-3-(2-methoxyphenyl)prop-2-en-1-one) ((E)-2-(3-(2,4-dimethoxyphenyl)acryloyl) -3H-benzo[f]chromen-3-one	783 1550 694 467 8.35	CAM-B3LYP/6-31 + G* CAM-B3LYP/6-31 + G* CAM-B3LYP/6-31 + G* LCwPBE/6-311G** BMK/6-311G**	This work This work [39]/2016 [6]/2018
glycine glycinium picrate	427	B3LYP/6-31G*	[17]/2018

Table 5

TD-DFT results of all studied compounds including their total dipole moments (μ_{tot}), transition energies ΔE (eV), oscillator strengths (f_0) and major orbital contributions.

Compounds	μ_{tot} (Debye)	ΔE (eV)	f_0	Major contribution	% C·I.
2a	2.723	6.119	0.760	$H-2 \rightarrow L+7$	26
2b	4.379	5.541	0.479	H-2 \rightarrow L+1	72
2c	3.788	6.113	0.847	H-2 \rightarrow L+1	12



Fig. 8. Calculated UV–Visible spectra of synthesized compounds 2a, 2b, and 2c.

4. Conclusion

In this study, 2-(1H-Benzo[d]imidazole-2-ylthio)-N-substitutedacetamides, were designed, synthesized and characterized by FT-IR, NMR spectroscopy and MS spectrometry. Geometric optimizations, vibrational frequencies, ¹H NMR chemical shifts have been estimated using the density functional theory methods with B3LYP functional and 6-31G(d) basis set, which supports the solid-state structures of the studied molecules. The theoretically calculated values of vibrational frequencies and chemical shifts are found to be consistent with the experimentally observed values. Theoretical findings reveal that the studied molecule 2c has strong absorption of UV light at 224 nm, because of the electron withdrawing ability of -NO2 substitution with higher β_0 value, amounted to 1550 au. Moreover, it can be concluded that the discussed experimental and theoretical parameters can be used to characterize the various thiazolo[3,2-a]benzimidazole based bioactive derivatives. By utilizing the above methods and substitution of electron rich/deficient moieties on these types of compounds could provide efficient NLO materials.

Conflicts of interest

There are no conflicts of interest to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2019.107742.

References

- Schneider T. Nonlinear optics in telecommunications. Springer Science & Business Media; 2013.
- [2] Papadopoulos MG, Sadlej AJ, Leszczynski J. Non-linear optical properties of matter. The Netherlands: Springer; 2006.
- [3] Ju C, Zhou Y, Semin S, Yang G, Tinnemans P, Duan Y, et al. Solvent dependent linear and nonlinear optical properties of triphenylamine unit incorporated difluoroboron β-diketonate complexes. Dyes Pigments 2019;162:776–85.
- [4] Newell A, Moloney J. Nonlinear optics. CRC Press; 2003.
- [5] Muhammad S, Xu H-L, Zhong R-L, Su Z-M, Al-Sehemi AG, Irfan A. Quantum chemical design of nonlinear optical materials by sp2-hybridized carbon nanomaterials: issues and opportunities. J Mater Chem C 2013;1(35):5439–49.
- [6] Shkir M, Muhammad S, AlFaify S, Irfan A, Patil PS, Arora M, et al. An investigation on the key features of a D-π-A type novel chalcone derivative for opto-electronic applications. RSC Adv 2015;5(106):87320–32.
- [7] Muhammad S, Al-Sehemi AG, Pannipara M, Irfan A. Design, characterization and nonlinear optical properties of coumarin appended chalcones: use of a dual approach. Optik 2018;164:5–15.
- [8] Muhammad S, Kumar S, Koh J, Saravanabhavan M, Ayub K, Chaudhary M. Synthesis, characterisation, optical and nonlinear optical properties of thiazole and benzothiazole derivatives: a dual approach. Mol Simul 2018;44(15):1191–9.
- [9] Ju C, Li X, Yang G, Yuan C, Semin S, Feng Y, et al. Polymorph dependent linear and nonlinear optical properties of naphthalenyl functionalized fluorenones. Dyes Pigments 2019;166:272–82.
- [10] Li X, Semin S, Estrada LA, Yuan C, Duan Y, Cremers J, et al. Strong optical nonlinearities of self-assembled polymorphic microstructures of phenylethynyl functionalized fluorenones. Chin Chem Lett 2018;29(2):297–300.
- [11] Kim MK, Shin H, Park K-S, Kim H, Park J, Kim K, et al. Benzimidazole derivatives as potent JAK1-selective inhibitors. J Med Chem 2015;58(18):7596–602.
- [12] Obot IB, Edouk UM. Benzimidazole: small planar molecule with diverse anti-corrosion potentials. J Mol Liq 2017;246:66–90.
- [13] Demirayak Ş, Abu Mohsen U, Çağri Karaburun A. Synthesis and anticancer and anti-HIV testing of some pyrazino[1,2-a]benzimidazole derivatives. Eur J Med Chem 2002;37(3):255–60.
- [14] Muhammad S, Xu H, Janjua MRSA, Su Z, Nadeem M. Quantum chemical study of benzimidazole derivatives to tune the second-order nonlinear optical molecular switching by proton abstraction. Phys Chem Chem Phys 2010;12(18):4791–9.
- [15] Yu J, Cui Y, Gao J, Wang Z, Qian G. Enhanced optical nonlinearity and improved transparency of Inorganic – Organic hybrid materials containing benzimidazole chromophores. J Phys Chem B 2009;113(45):14877–83.
- [16] Yadav S, Lim SM, Ramasamy K, Vasudevan M, Shah SAA, Mathur A, et al. Synthesis and evaluation of antimicrobial, antitubercular and anticancer activities of 2-(1benzoyl-1H-benzo[d]imidazole-2-ylthio)-N-substituted acetamides. Chem Cent J 2018;12(1):66.

- [17] Mao R, Shao J, Zhu K, Zhang Y, Ding H, Zhang C, et al. Potent, selective, and cell active protein arginine methyltransferase 5 (PRMT5) inhibitor developed by structure-based virtual screening and hit optimization. J Med Chem 2017;60(14):6289–304.
- [18] Mavrova AT, Anichina KK, Vuchev DI, Tsenov JA, Denkova PS, Kondeva MS, et al. Antihelminthic activity of some newly synthesized 5(6)-(un)substituted-1H-benzimidazol-2-ylthioacetylpiperazine derivatives. Eur J Med Chem 2006:41(12):1412–20.
- [19] Muhammad S, Al-Sehemi AG, Irfan A, Chaudhry AR. Tuning the push–pull configuration for efficient second-order nonlinear optical properties in some chalcone derivatives. J Mol Graph Model 2016;68:95–105.
- [20] Shkir M, Muhammad S, AlFaify S, Irfan A, Khan MA, Al-Sehemi AG, et al. A comparative study of key properties of glycine glycinium picrate (GGP) and glycinium picrate (GP): a combined experimental and quantum chemical approach. J Saudi Chem Soc 2018;22(3):352–62.
- [21] Shirata K, Kawauchi S. Effect of benzimidazole configuration in polybenzimidazole chain on interaction with phosphoric acid: a DFT study. J Phys Chem B 2015:119(2):592–603.
- [22] Pina J, Seixas de Melo JS, Batista RMF, Costa SPG, Raposo MMM. Triphenylamine–benzimidazole derivatives: synthesis, excited-state characterization, and DFT studies. J Org Chem 2013;78(22):11389–95.
- [23] Sas EB, Cevik M, Kurt M. Experimental and theoretical analysis of 2-amino 1-methyl benzimidazole molecule based on DFT. J Mol Struct 2017;1149:882–92.
- [24] Su F, Sun Z, Su W, Liang X. NMR investigation and theoretical calculations on the tautomerism of benzimidazole compounds. J Mol Struct 2018;1173:690–6.
- [25] Tayade RP, Sekar N. Benzimidazole-thiazole based NLOphoric styryl dyes with solid state emission - synthesis, photophysical, hyperpolarizability and TD-DFT studies. Dyes Pigments 2016;128:111–23.
- [26] Gao Y, Zhong R-L, Xu H-L, Sun S-L, Su Z-M. The effect of ring sizes and alkali metal cations on interaction energy, charge transfer and nonlinear optical properties of crown ether derivatives. RSC Adv 2015;5(38):30107–19.
- [27] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 09 rev B01. Wallingford, CT: Gaussian, Inc.; 2009.
- [28] Quick A, Williams DJ. The crystal structure of the complex salt: benzimidazole benzimidazolium fluoroborate. Can J Chem 1976;54(15):2482–7.
- [29] Bai Y, Lv X, Liu Z, Guo T, Li J. Synthesis, spectral and DFT study of 5-butyl-3,9difluoro-5H-benzimidazo[1,2-a]benzimidazole. J Mol Struct 2018;1151:117–25.
- [30] Karnan M, Balachandran V, Murugan M. FT-IR, Raman and DFT study of 5-chloro-4nitro-o-toluidine and NBO analysis with other halogen (Br, F) substitution. J Mol Struct 2013;1039:197–206.
- [31] Lokaj J, Kettmann V, Milata V, Solcan T. 5-Amino-1-methyl-1H-benzimidazole.

Acta Crystallogr E 2009;65(8):01788.

- [32] Morsy MA, Al-Khaldi MA, Suwaiyan A. Normal vibrational mode analysis and assignment of benzimidazole by ab initio and density functional calculations and polarized infrared and Raman spectroscopy. J Phys Chem A 2002;106(40):9196–203.
- [33] Wilson EB. The normal modes and frequencies of vibration of the regular plane hexagon model of the benzene molecule. Phys Rev 1934;45(10):706–14.
- [34] Champagne B, Plaquet A, Pozzo J-L, Rodriguez V, Castet F. Nonlinear optical molecular switches as selective cation sensors. J Am Chem Soc 2012;134(19):8101–3.
 [35] Gao F-W, Zhong R-L, Sun S-L, Xu H-L, Su Z-M. Two-electron/24-center (2e/24c)
- bonding in novel diradical π-dimers. Phys Chem Chem Phys 2016;18(42):29041–4.
 [36] Chen S, Sun S-L, Wu H-Q, Xu H-L, Zhao L, Su Z-M. Superatoms (Li3O and BeF3) induce phenalenyl radical π-dimer: fascinating interlayer charge-transfer and large NLO responses. Dalton Trans 2014;43(33):12657–62.
- [37] Zhong R-L, Xu H-L, Su Z-M. Connecting effect on the first hyperpolarizability of armchair carbon-boron-nitride heteronanotubes: pattern versus proportion. Phys Chem Chem Phys 2016;18(20):13954–9.
- [38] Muhammad S, Xu H, Su Z, Fukuda K, Kishi R, Shigeta Y, et al. A new type of organic-inorganic hybrid NLO-phore with large off-diagonal first hyperpolarizability tensors: a two-dimensional approach. Dalton Trans 2013;42(42):15053–62.
- [39] Muhammad S, Al-Sehemi AG, Su Z, Xu H, Irfan A, Chaudhry AR. First principles study for the key electronic, optical and nonlinear optical properties of novel donoracceptor chalcones. J Mol Graph Model 2017;72:58–69.
- [40] Muhammad S, Nakano M, Al-Sehemi AG, Irfan A, Chaudhry AR, Tonami T, et al. Exploring the novel donor-nanotube archetype as an efficient third-order nonlinear optical material: asymmetric open-shell carbon nanotubes. Nanoscale 2018;10(35):16499–507.
- [41] Muhammad S, Al-Sehemi AG, Irfan A, Chaudhry AR, Gharni H, AlFaify S, et al. The impact of position and number of methoxy group(s) to tune the nonlinear optical properties of chalcone derivatives: a dual substitution strategy. J Mol Model 2016;22(4):73.
- [42] Muhammad S. Second-order nonlinear optical properties of dithienophenazine and TTF derivatives: a butterfly effect of dimalononitrile substitutions. J Mol Graph Model 2015;59:14–20.
- [43] Muhammad S, Al-Sehemi AG, Irfan A, Algarni H, Qiu Y, Xu H, et al. The substitution effect of heterocyclic rings to tune the optical and nonlinear optical properties of hybrid chalcones: a comparative study. J Mol Graph Model 2018;81:25–31.
- [44] Muhammad S, Irfan A, Shkir M, Chaudhry AR, Kalam A, AlFaify S, et al. How does hybrid bridging core modification enhance the nonlinear optical properties in donor-π-acceptor configuration? A case study of dinitrophenol derivatives. J Comput Chem 2015;36(2):118–28.