**Structural, Electronic and Nonlinear Optical Properties of Novel Derivatives of 9,12-diiodo-1,2-dicarba-closo-dodecaborane: Density Functional Theory Approach**

Aijaz Rasool Chaudhrya,[[1]](#footnote-1),Shabbir Muhammadb,c, Ahmad Irfanc,d, Abdullah G. Al- Sehemic,d,,Bakhtiar Ul Haqb,c, Sajjad Hussaine

*a Deanship of Scientific Research, University of Bisha, Bisha 61922, P.O. Box 551, Saudi Arabia*

*b Department of Physics, College of Science, King Khalid University, Abha 61413, P.O. Box 9004, Saudi Arabia*

*c Research Center for Advanced Materials Science (RCAMS), King Khalid University, Abha 61413, P.O. Box 9004, Saudi Arabia*

*d Department of Chemistry, Faculty of Science, King Khalid University, Abha 61413, P.O. Box 9004, Saudi Arabia*

*e Henan Key Laboratory of Boron Chemistry and Advanced Energy Materials, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, 453007, China*

**Abstract**

Using density functional theory (DFT) methods, we shed light on the structural, optical, electronic and nonlinear optical (NLO) properties of three derivatives of 9,12-diiodo-1,2-dicarba-closo-dodecaborane (12) (C2H10B10I2). The DFT and TD-DFT methods are considered very precise and practical to optimize the ground and excited state geometries, respectively. A vibrant intra-molecular charge transfer from highest occupied molecular orbitals (HOMOs) to the lowest unoccupied molecular orbitals (LUMOs) was observed in all compounds. The geometrical parameters of experimental crystal structure, i.e., bond lengths/angles have been successfully reproduced. The HOMO and LUMO energies, as well as their energy gaps (Eg) were also calculated and compared with each other for all derivatives. The effect of attached groups on electronic, optical and NLO properties along with detailed structure-property relationship was discussed. For nonlinear optical (NLO) response, the CAM-B3LYP functional along with relatively larger basis set 6-31+G\*\* (for hydrogen, carbon, boron and oxygen atoms) and LANL2DZ (for Iodine atoms) have been used to optimize the compounds at ground states. The calculation of second-order NLO polarizabilities (*β*tot) shows that compounds **2** and **3** possess the *β*tot amplitudes of 3029 and 4069 a. u., respectively, with CAM-B3LYP method which are reasonably larger than similar prototype molecules. Owing to their unique V-shapes, the nonlinear anisotropy values are found to be 0.63, 0.34 and 0.44 for compounds **1-3**, respectively, which show the significant two-dimensional character of these compounds. Thus, the NLO amplitudes as well as nonlinear anisotropies indicate that the above-entitled compounds are good contenders for optical and NLO applications.

***Keywords*:** Decaboranes; Semiconductors; Density functional theory; Electronic properties; NLO application.

*1. Introduction*

Iodine (I) substituted at boron (B) atoms in carboranes has been intensively studied as precursors of large number of B-carboranes [[1-3](#_ENREF_1)]. Structural properties of some B-iodo-carboranes were also investigated [[4-6](#_ENREF_4)]. Previously, Boron based 9,12-Diiodo-1,2-dicarba-closo-dodecaborane (12) (C2H10B10I2) has been reported [[7](#_ENREF_7)] as an individual compound for structural properties of this fascinating compound. Several iodinated ortho-carborane crystal structures were comprehensively investigated during the last few years and revealed the diversity of intermolecular interactions, which these materials may adopt in the solid state [[8](#_ENREF_8)]. Furthermore, these fascinating complexes have been reported as stable compounds to several chemical conditions and also illustrate a huge potential to incorporate with a several substituents. The ortho-carboranes (1,2-dicarba-closododecaboranes) had been described as a prospective building blocks in supramolecular chemistry [[9](#_ENREF_9), [10](#_ENREF_10)]. Although a large number of iodinated carboranes and decaboranes are available, still they have a lot of potentials to be explored, especially the nonlinear optical (NLO) response of these compounds. Previously, it has been shown that due tobetter phase matching and increased stability two-dimensional (2D) chromophores having large off-diagonal *β*-tensor components have advantage over 1D chromophores [[11](#_ENREF_11), [12](#_ENREF_12)].Nowadays, compounds with great off-diagonal *β* tensor components are being recommended as they can offer large macroscopic NLO responses. Hitherto, NLO properties of numerous 2D compounds were studied by substituting donor and/or acceptor (D/A) in V-shaped molecules [[12](#_ENREF_12), [13](#_ENREF_13)]. It was shown that angle between the intramolecular charge transfer (ICT) axis is important parameter to check the relative magnitude of off-diagonal and diagonal components. In current study of dicarba-closo-dodecaborane derivatives, the CT comprises both sides of dicarba-closo-dodecaborane. Additionally, Coe *et al.* work showed that large off-diagonal *β* tensor components are intensely interconnected to oscillator strength, low-lying energy excited states with the electron transition dipole moment between two states that are perpendicular to the dipolar axis [[13](#_ENREF_13)].

Earlier, ICT has been studied through bridging effect on first hyperpolarizability [[14](#_ENREF_14)]. In some other studies NLO response properties of various ICT compounds were explored [[15-17](#_ENREF_15)].There is great demand to improve new organic–inorganic hybrid compounds that can associate benefits of organic materials (high NLO efficiency) as well as inorganic materials (good stability, wide transparency range). Owing to good thermal stability of dicarba-closo-dodecaborane and its versatile nature, they are being used in various functional materials [[18](#_ENREF_18)]. It is anticipated that due to V-shaped structures of dicarba-closo-dodecaborane derivatives might lead to better NLO properties. In current study, we have designed organic-inorganic hybrid proficient NLO-phores. The present investigations aim to explore the structure-property relationship of V-shaped dicarba-closo-dodecaborane derivatives and their potential as NLO-phores.

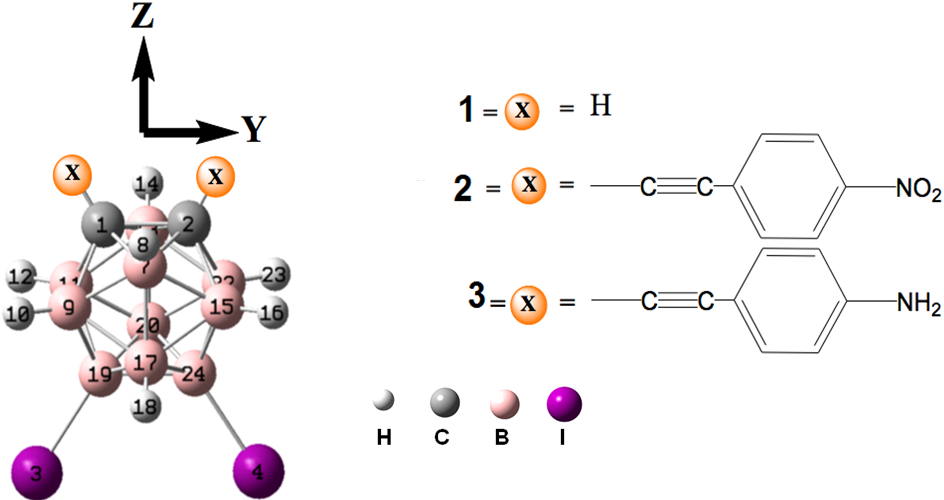
The nonlinear response properties are characterized by second- and third-order polarizabilities. The NLO materials have important applications in many fields of modern hi-tech society including optical data processing and frequency doubling etc. Over the past some years, our group has reported many compounds with efficient NLO response [[19](#_ENREF_19), [20](#_ENREF_20)]. Similar to our several previous studies [[21](#_ENREF_21)], we have calculated the static total second-order polarizabilities **(***β*tot**)** of compounds **1-3** to check their possible NLO response. Furthermore, a comparison of *β*tot and *β*vec has been done and presented in Table 5 of section 3.4 of results and discussion.

It is also important to mention that the amplitude of *β*tot is always positive irrespective of the sign of individual tensorial components which cannot be measured experimentally. Whereas, the amplitude of *β*vec may be positive or negative depending on the direction of dipole moment and charge transfer process for typical molecular system [[15](#_ENREF_15), [22](#_ENREF_22)]. The relation between *βvec* and *βtot* presents essential evidence about the direction of charge transfer in the molecules [[15](#_ENREF_15), [23](#_ENREF_23)] and specified by equation:

In above equation, θ is the angle among vector formed by βvec components and the dipole moment vector. Usually, this ratio near to 1 indicates a unidirectional charge transfer within the molecular systems where *β*tot and *β*vec carry the similar amplitudes.

In the present study, we have selected 9,12-Diiodo-1,2-dicarba-closo-dodecaborane (12) (C2H10B10I2) [[7](#_ENREF_7)] as parent molecule (named as **1** in the text) and derived two new compounds (**2** and **3**, respectively) with the aim to tune the optoelectronic and nonlinear optical (NLO) properties. In compound **2**, 1-nitro-4-propynyl-benzene group was substituted at X-positions; while in compound **3** 1-amino-4-propynyl-benzene has been attached at X-positions of the parent compound (**1**), see Fig. 1. The purpose of substituting 1-nitro-4-propynyl-benzene group (strong electron acceptor) and 1-amino-4-propynyl-benzene (strong electron donor) at X-positions of the parent compound is to explore the effect of acceptor and donor ligands on various properties of interest, respectively. Both the 1-nitro-4-propynyl-benzene group and 1-amino-4-propynyl-benzene groups are representative of the best electron donor and electron acceptor groups, respectively, which are often used as prototypes to check the electron donor-acceptor effects in push-pull molecules.[[24](#_ENREF_24)] The above-mentioned groups are used as general representative of acceptor and donor moieties of compounds to establish the electronic communication with 9,12-Diiodo-1,2-dicarba-closo-dodecaborane (12). We have explored the structural, frontier molecular orbitals, optical spectra (absorption (λa) and emission (λe)) as well as NLO properties of targeted compounds by density functional theory (DFT) [[25](#_ENREF_25)] and time dependent DFT (TD-DFT) [[26-29](#_ENREF_26)]. Moreover, the *β*tot and *β*vec values of the studied compounds **1-3** have been evaluated in detail to understand the direction of charge transfer in the molecules.

A contemporary survey of literature showed that there is no such computational study carried out heretofore on these studied compounds. This is the first time that we are going to have an in-depth study of 9,12-diiodo-1,2-dicarba-closo-dodecaborane (12) (C2H10B10I2) and two of its novel derivatives, see Fig. 1.



**Fig. 1:** The optimized structures and schematic diagram of all derivatives investigated in the current study.

*2. Computational details*

In the present study, B3LYP method was adopted to optimize the ground state S0 geometries of molecules because the hybrid functional B3LYP of DFT has been widely used to reproduce the experimental electronic [[30](#_ENREF_30), [31](#_ENREF_31)] and geometric parameters [[32-38](#_ENREF_32)]. The basis set Gen is a hybrid basis set including 6-31G\*\* for hydrogen, carbon, boron and oxygen atoms, while LANL2DZ for Iodine atoms. Preat et al. revealed that B3LYP method is suitable for the ground state (S0) geometry optimizations [[39](#_ENREF_39), [40](#_ENREF_40)]. Moreover, Huong and co-workers confirmed that the B3LYP/6-31G\*\* level is decent approach to reproduce the experimental crystal data as well as rational for the electronic and charge transport properties [[41](#_ENREF_41)]. The excited state (S1) geometries were optimized at TD-DFT [[42](#_ENREF_42)] using the TD/B3LYP/6-31G\*\* (LANL2DZ) level of theory. Then the same TD-DFT level was applied to evaluate the absorption and emission spectra which already verified to be a proficient method [[29](#_ENREF_29)]. It is important to note down here that many critical studies indicated that B3LYP is not appropriate for the calculation of NLO polarizabilities as reported by Champagn et al.[[43](#_ENREF_43), [44](#_ENREF_44)]. Recently, Misra et al.[[15](#_ENREF_15)] reported that the CAM-B3LYP and MP2 are suitable to calculate the NLO response, whereas the CAM-B3LYP is considered more appropriate for NLO response without compromising the computing cost and accuracy. Previously, the hybrid functional CAM-B3LYP has been reported as useful for evaluating the NLO response of several charge transfer base molecule [[45-47](#_ENREF_45)]. To overcome such discrepancies, we have also optimized the compounds **1-3** at CAM-B3LYP method along with relatively larger basis set 6-31+G\*\* (LANL2DZ) for ground state. The static second-order polarizabilities at CAM-B3LYP/6-31+G\*\* (LANL2DZ) have been evaluated for compounds **1-3** initially optimized atB3LYP/6-31G\*\* (LANL2DZ) level of theory and are tabulated in Table 5and S2 of supporting information. Furthermore, we also compute the static second-order polarizabilities at CAM-B3LYP/6-31+G\*\* (LANL2DZ) for compounds **1-3** optimized at the same level of theory and presented in Table 5.

It is found that there are noticeable differences among the amplitudes of *β*tot and βvec at different levels of theory. At two different levels of theory (B3LYP vs. CAM-B3LYP), the approximate percentage differences among amplitudes of *β*tot and βvec are found to be 32, 50 and 14% for compounds **1**, **2** and **3**, respectively. A detailed analysis is given in Table S1 of supporting information.

A well-known finite field (FF) approach combined with DFT method is used for the calculation of NLO response. In FF method, a static electric field (*F*) is applied and the energy (*E*) of the molecule is given by following Eq.

where, *i*, *j* and *k* labels the *x*, *y* and *z* components, respectively. The total energy of molecule is represented by *E*(0) withoutany field while μ and α are the dipole moment and linear polarizability. Similarly, the β and γ are the second- and third-order nonlinear polarizabilities, respectively. It is obvious from equation (1) that differentiating E with respect to F attains the 27 components of *β*. According to Kleinman symmetry (βxyy = βyxy = βyyx, βyyz = βyzy = βzyy,… likewise other permutations also take same value). So, the 27 components of second-order nonlinear polarizability (*β*) can be reduced to 10 components.

The value of *β*tot and *β*vec are calculated by the following equations:

(2)

where

(3)

(4)

(5)

(6)

All these quantum chemical calculations were performed using Gaussian09 package [[48](#_ENREF_48)].

**3. Results and discussion**

*3.1. Molecular Geometries*

The S0 and S1 significant geometrical parameters, i.e., bond lengths (Å) and bond angles (degrees, 0) of parent borane compound **1** and its derivatives **2** and **3** at B3LYP/Gen and TD-B3LYP/Gen levels of theory are tabulated in Tables 1, 2, 3 and 4. It can be seen from Tables 1 and 2 that the computed S0 bond lengths and bond angles were found in reasonable agreement with the experimental crystal structural geometric parameters. The bond lengths I3-B19, I4-B24, C2-B13, B20-B19 and B9-B19 were being overestimated, i.e., 0.014, 0.025, 0.014, 0.016 and 0.018 Å, respectively, for compound **1;** 0.011, 0.021, 0.042, 0.034, 0.014 and 0.019 Å for compound **2**, for compound **3**, the increase in the bond lengths are as 0.017, 0.027, 0.030, 0.013 and 0.026 Å, respectively, as compared to the experimental data. The increase in the bond lengths is because of the experimental geometrical data is in the solid phase whereas the computed parameters are in gas phase. The alteration in the bond angles I3-B19-B9, I3-B19-B9-I4-B24-B17 and I4-B24-B17 was observed as 2.980, -2.510, 1.170 and 2.10 for parent compound **1**; 3.30, -2.830, 1.50 and 2.40 for compound **2,** while 3.430, -2.990, 1.640 and 2.550 for compound **3**, respectively in comparison to experimental data.

Here, the lengthening or shortening in the bond lengths, as well as variation in the bond angles from S0 to S1 was also discussed. In compounds **1-3**,the lengthening from the S0 to S1 was 0.096, 0.086 and 0.018 Å for I3-B19 and I4-B24 bond lengths, respectively. For B7-B17bond length, the shortening was determined 0.049, 0.027 and 0.09 Å in **1-3** from S0 to S1, respectively. While for B11-B9bond length, the lengthening was noticed from S0 to S1, i.e., 0.073, 0.029 and 0.007 Å in **1-3**, respectively. The bond angle I3-B19-B24 decreases 11.100, 9.560 and 1.600; the bond angle I3-B19-B11 increased by 100, 4.540 and 5.020; the bond angle I3-B19-B20 decreases 8.510, 2.460 for **1** and **2**, whereas increased for **3** as 1.640. The variation in the bond angles I3-B19-B17, I3-B19-B9, I4-B24-B19, I4-B24-B17, I4-B24-B15, I4-B24-B22, I4-B24-B20 and B7-C1-B9 from S0 to S1 was found as -5.960, 4.730, -11.790, -8.520 , 10.010, 6.520 , -5.980 and -0.820 for **1**; For **2** as -2.450, 4.690, -9.570, -2.460 , 4.60, 4.60 , -2.450 and 4.980, however for the derivative **3** the alteration in the above mentioned bond angles has been evaluated as 1.620, -1.10, -1.770, 1.530 , -1.980, -1.940 , 1.530 and 7.130, respectively. From these variations in the bond angle red shift behavior from S0 to S1 can be predicted for compounds **1-3.**

**Table 1:** Selected optimized bond lengths (Angstrom, Å) and bond angles (degree, 0) of ground state for Borane derivatives at the B3LYP/Genb levels of theory, respectively.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Parameters | **Exp.a** | **1** | **2** | **3** |
| I3-B19 | 2.183 | 2.197 | 2.194 | 2.200 |
| I4-B24 | 2.173 | 2.198 | 2.194 | 2.200 |
| C1-B9 | 1.697 | 1.697 | 1.703 | 1.690 |
| C1-B7 | 1.723 | 1.718 | 1.738 | 1.734 |
| C2-B22 | 1.690 | 1.697 | 1.703 | 1.690 |
| C2-B13 | 1.704 | 1.718 | 1.738 | 1.734 |
| B7-B17 | 1.764 | 1.764 | 1.765 | 1.773 |
| B7-B9 | 1.786 | 1.777 | 1.783 | 1.789 |
| B11-B19 | 1.774 | 1.777 | 1.776 | 1.776 |
| B11-B20 | 1.790 | 1.782 | 1.778 | 1.776 |
| B11-B9 | 1.789 | 1.789 | 1.791 | 1.790 |
| B20-B13 | 1.773 | 1.764 | 1.765 | 1.773 |
| B20-B19 | 1.780 | 1.796 | 1.794 | 1.793 |
| B13-B22 | 1.773 | 1.777 | 1.765 | 1.789 |
| B15-B24 | 1.774 | 1.777 | 1.776 | 1.776 |
| B15-B22 | 1.790 | 1.789 | 1.791 | 1.790 |
| B9-B19 | 1.795 | 1.777 | 1.776 | 1.775 |
| B20-B24 | 1.792 | 1.796 | 1.794 | 1.793 |
| I3-B19-B24 | 124.10 | 124.21 | 124.23 | 124.10 |
| I3-B19-B11 | 119.70 | 119.69 | 119.47 | 119.25 |
| I3-B19-B20 | 119.20 | 122.18 | 122.50 | 122.63 |
| I3-B19-B17 | 121.80 | 122.18 | 122.50 | 122.65 |
| I3-B19-B9 | 122.20 | 119.69 | 119.37 | 119.21 |
| I4-B24-B19 | 123.30 | 124.21 | 124.24 | 124.10 |
| I4-B24-B17 | 121.00 | 122.17 | 122.50 | 122.64 |
| I4-B24-B15 | 119.15 | 119.68 | 119.40 | 119.25 |
| I4-B24-B22 | 119.10 | 119.69 | 119.40 | 119.21 |
| I4-B24-B20 | 120.10 | 122.20 | 122.50 | 122.65 |
| B7-C1-B9 | 62.83 | 62.70 | 62.43 | 62.98 |

*a* Experimental (Exp.) data of (compound **1**) from reference [[7](#_ENREF_7)].

bGen = 6-31G\*\* for H, C, B and O atoms, while Gen = LANL2DZ for I atoms

**Table 2:** Selected optimized bond lengths (Angstrom, Å) and bond angles (degree, 0) of excited state for Borane derivatives at the B3LYP/Genb levels of theory, respectively.

|  |  |  |  |
| --- | --- | --- | --- |
| Parameters | **1** | **2** | **3** |
| I3-B19 | 2.293 | 2.280 | 2.218 |
| I4-B24 | 2.293 | 2.280 | 2.212 |
| C1-B9 | 1.687 | 1.640 | 1.645 |
| C1-B7 | 1.695 | 1.640 | 1.693 |
| C2-B22 | 1.687 | 1.640 | 1.623 |
| C2-B13 | 1.695 | 1.640 | 1.623 |
| B7-B17 | 1.715 | 1.792 | 1.764 |
| B7-B9 | 1.739 | 1.836 | 1.843 |
| B11-B19 | 1.799 | 1.770 | 1.762 |
| B11-B20 | 1.810 | 1.773 | 1.764 |
| B11-B9 | 1.853 | 1.820 | 1.797 |
| B20-B13 | 1.715 | 1.792 | 1.843 |
| B20-B19 | 1.770 | 1.794 | 1.809 |
| B13-B22 | 1.739 | 1.836 | 1.863 |
| B15-B24 | 1.800 | 1.770 | 1.778 |
| B15-B22 | 1.853 | 1.820 | 1.828 |
| B9-B19 | 1.732 | 1.770 | 1.762 |
| B20-B24 | 1.786 | 1.794 | 1.804 |
| I3-B19-B24 | 112.43 | 114.67 | 122.50 |
| I3-B19-B11 | 129.70 | 124.01 | 124.27 |
| I3-B19-B20 | 113.66 | 120.05 | 118.12 |
| I3-B19-B17 | 116.22 | 120.05 | 124.27 |
| I3-B19-B9 | 126.53 | 124.01 | 118.11 |
| I4-B24-B19 | 112.42 | 114.67 | 122.33 |
| I4-B24-B17 | 113.65 | 120.05 | 124.17 |
| I4-B24-B15 | 129.69 | 124.01 | 117.27 |
| I4-B24-B22 | 126.52 | 124.01 | 117.27 |
| I4-B24-B20 | 116.22 | 120.05 | 124.18 |
| B7-C1-B9 | 61.88 | 67.41 | 70.11 |

*a* = Experimental (Exp.) data of (Compound **1**) from reference [[7](#_ENREF_7)].

bGen = 6-31G\*\* for H, C, B and O atoms, while Gen = LANL2DZ for I atoms

*3.2. Electronic properties*

The ground state as well as excited state energies of the frontier molecular orbitals (FMOs) and energy gaps of Borane based derivatives compounds **1-3** have been tabulated in Table 3. The ground state and excited state HOMO energies (*E*HOMO), LUMO energies (*E*LUMO) and HOMO-LUMO energy gaps (*Eg*) of compounds **1-3** were calculatedat B3LYP/6-31G\*\* and TD-B3LYP/6-31G\*\* levels of theory, respectively which are tabulated in Table 3. The trend in the *E*HOMO is **3** > **1,** > **2,** while in the *E*LUMO is **1** > **3** > **2,** for the ground and excited states. The tendency in the *Eg* was observed as **1** > **3** > **2** at ground state while **1 > 2 > 3** at excited state. Here electron and hole injection energies were calculated to understand the charge injection behavior of the studied derivatives. The electron injection energy was calculated as (=−*E*LUMO − (−work function of metal)). The work function of aluminum (Al) is −4.08 eV. The electron injection energy was found 3.24 eV (=−0.84 − (−4.08)), 0.75 eV (=−3.33 − (−4.08)), and 2.19 eV (=−1.89 − (−4.08)) from the compounds **1- 3** to Al electrode, respectively. It is expected that **2** might be better electron transport contender having the smallest electron injection barrier to Al electrode. Moreover, thesmaller and low-lying*E*LUMO of **2** than other counterparts revealed that prior compound might be thermodynamically more stable and charge transport can’t be quenched by losing the electrons. The hole injection energy of compounds **1-3** has been predicted, i.e., 2.55 eV (=−4.08 − (−6.63)), 2.71 eV (=−4.08 − (−6.79)) and 1.70 eV (=−4.08 − (−5.78)) from compounds **1-3** to the Al electrode, respectively. It is expected that **3** would be better hole transport material. The charge distribution patterns of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of Boron based derivatives **1-3** have been illustrated in Fig. 2 for ground states, while for excited states the HOMO and LUMO formations have been shown in Fig. S2 of supporting information.

**Table 3**

The HOMO energies (*E*HOMO), LUMO energies (*E*LUMO), and HOMO-LUMO energy gaps (*E*g) in eV for ground and first excited states computed at the B3LYP/Genb and TD-B3LYP/Genb level of theories, respectively.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Complexes | Ground states | | | First excited states | | |
| *EHOMO* | *ELUMO* | *Eg* | *EHOMO* | *ELUMO* | *Eg* |
| **1** | -6.63 | -0.84 | 5.78 | -5.73 | -3.61 | 2.12 |
| **2** | -6.79 | -3.33 | 3.47 | -6.10 | -4.37 | 1.73 |
| **3** | -5.78 | -1.89 | 3.89 | -5.27 | -3.65 | 1.62 |

bGen = 6-31G\*\* for H, C, B and O atoms, while Gen = LANL2DZ for I atoms

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**Fig. 2:** Distribution patterns of the HOMOs and LUMOs of compounds **1-3** at the ground states.

*3.3. Optical properties*

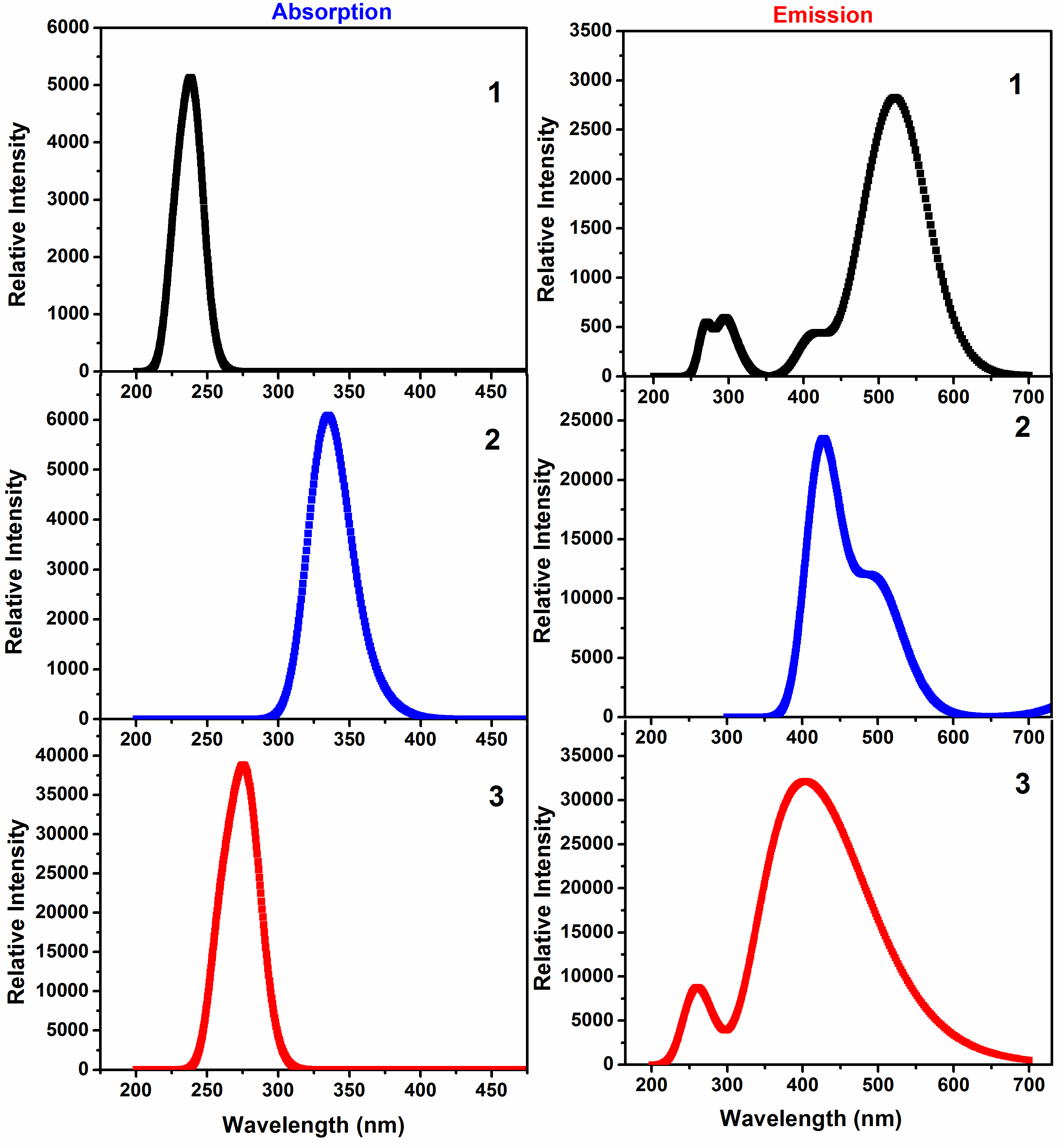
The maximum absorption wavelengths (λa), emission wavelengths (λe), oscillator strengths (ƒ) and major transitions involved at TD-B3LYP/6-31G\*\* (LANL2DZ) level of theory have been tabulated in Table 4 and Fig. 3. It has been observed that by introducing the 1-nitro-4-propynyl-benzene at X-positions of the parent compound leads to 92 nm red shift as in **2** inλa. Moreover, the introduction of 1-amino-4-propynyl-benzene at X-positions of the parent compound leads to 35 nm red shift (**3**) in λa. The maximumλa peaks of compounds **1-3** were observed at 241, 333 and 276 nm with the major transitions H-1 → L, H-3 → L+1 and H-1 → L, respectively. It was also found that introduction of 1-nitro-4-propynyl-benzene at X-positions of the parent compound leads to 106 nm blue shift as in **2** in λe. Moreover, the introduction of 1-amino-4-propynyl-benzene at X-positions of the parent compound leads to 33 nm red shift (**3**) in λe. The maximumλe peaks of compounds **1-3** were observed at 532, 426 and 499 nm with the major transitions L → H-1, L → H-4 and L → H-5, respectively. The Stokes shift from the absorption to the emission wavelengths was observed 291, 93 and 223 nm for compounds **1-3**, respectively.

**Table 4**

The absorption (λa) and emission wavelengths (λe) (nm), oscillator strengths (*f*) and major transitions of compounds **1-3** calculated at TD-B3LYP/Genb level of theory

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Complexes | *f* | λa | Transition | *f* | λe | Transition |
| **1** | 0.0314 | 241 | H-1 → L | 0.0317 | 532 | L → H-1 |
| **2** | 0.0545 | 333 | H-3 → L+1 | 0.3169 | 426 | L → H-4 |
| **3** | 0.2649 | 276 | H-1 → L | 0.333 | 499 | L → H-5 |

bGen = 6-31G\*\* for H, C, B and O atoms, while Gen = LANL2DZ for I atoms



**Figure 3:** The absorption and emission spectra of compounds **1-3** calculated using TD-B3LYP/6-31G\*\*(LANL2DZ) level of theory

*3.4. Nonlinear optical properties*

We optimized compounds **1-3** at CAM-B3LYP/6-31+G\*\* (LANL2DZ) and B3LYP/6-31+G\*\* (LANL2DZ) levels of theory for ground neutral states. The static second-order polarizabilities along with their individual components have been also computed at B3LYP/6-31+G\*\* (LANL2DZ) and CAM-B3LYP/6-31+G\*\* (LANL2DZ) and given in Table 5 for comparison. In present investigation, we have calculated static total second-order polarizabilities (*β*tot)according to equations 2 to 5 as given in computational details (Section 2). From Table 5, it is seen that second-order polarizability values are dominated by their diagonal (*β*zzz) components among all other components. Comparatively higher amplitudes of characteristic components of the second-order polarizability illustrate a significant delocalization/transfer of charges around these directions. For example, in present case, the *z*-axis is the main axis of charge transfer (see Figure 1) and it has the highest *z*-components of βtot values in almost all the systems as given in Table 5.

At CAM-B3LYP/6-31+G\*\* (LANL2DZ) level, the parent compound **1** has *β*tot value of 552 a. u. that significantly increases in its derivatives in the order of **1** < **2** < **3**. The compounds **2** and **3** have *β*tot values of 3029 and 4069 a. u., which are 6 and 7 times larger than that of **1**, respectively. Similar trend was observed for compounds **1-3** with some overestimated values of *β*tot when B3LYP/6-31+G\*\* (LANL2DZ) optimized geometries were used to calculate the *β* at B3LYP/6-31+G\*\* (LANL2DZ) level of theory. The calculated *β*tot values were found to be 827, 6391 and 6789 a. u. for compounds **1**, **2** and **3**, respectively.

To further elucidate the origin of NLO in the compounds **1-3**, their individual diagonal and off-diagonal components have been also shown in Table 5. The diagonal components for all the compounds are along the charge transfer z-axis. The ratio (*η*) between diagonal (βzzz) and off-diagonal (βyyz) components is usually referred as nonlinear anisotropy, which important parameters for two-dimensional NLO chromophores. The two-dimensional NLO chromophores usually possess better phase matching and transparency etc. The NLO anisotropies at CAM-B3LYP are 0.63, 0.34 and 0.44 for compounds **1-3**, respectively, which show the significant two-dimensional character of these compounds. Thus, the NLO amplitudes and NLO anisotropies indicate that the above-entitled compounds might have significant potential to use them in NLO applications. Furthermore, a comparison of *β*tot and *β*vec also presented in Table 5 because the ratio of *β*vec and *β*tot also specifies important information about the direction of charge transfer in the molecules. Usually, this ratio near to 1 indicates a unidirectional charge transfer within the molecular systems where *β*tot and *β*vec carry the similar amplitudes. It is also important to mention that the amplitude of *β*tot always possess positive sign while on the other hands, the amplitude of *β*vec may be positive or negative depending on the direction of dipole moment and charge transfer process for typical molecular system.

The ratio of *β*vec and *β*tot have been calculated and is found to be 0.6 for compounds **1-3** computed at CAM-B3LYP level (CAM-B3LYP optimized structures were used). These smaller values specify that the charge transfer process in not unidirectional because of the V-shape of molecular systems, which lower the value of *β*vec as compared to the respective βtot amplitudes.

**Table 5.**

The calculated values of total second-order polarizabilities (βtot, a. u.)a, (βvec, a. u.)a along with their individual components for compounds **1-3** at B3LYP/Genb and CAM-B3LYP/Genb levels of theory, where geometries were also optimized using the same respective methods.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | **1** | | **2** | | **3** | |
| β | Optimized  at  B3LYP | Optimized  at  CAM-B3LYP | Optimized  at  B3LYP | Optimized  at  CAM-B3LYP | Optimized  at  B3LYP | Optimized  at  CAM-B3LYP |
| 6-31G\*\* | 6-31+G\*\* | 6-31G\*\* | 6-31+G\*\* | 6-31G\*\* | 6-31+G\*\* |
| βxxx | 5 | 6 | 4 | 15 | 2 | -3 |
| βxxy | 6 | 0 | 1 | 1 | -4 | 4 |
| βxyy | 1 | 0 | -41 | -22 | 0 | 19 |
| βyyy | 7 | 0 | -101 | -28 | 94 | -204 |
| βxxz | 94 | -3 | -31 | -193 | 276 | 80 |
| βxyz | 1 | -2 | -24 | 23 | -72 | 17 |
| βyyz | 238 | 215 | 1587 | 818 | 2760 | 1256 |
| βxzz | 1 | -1 | -129 | -72 | -5 | 41 |
| βyzz | 8 | 0 | -20 | -7 | -19 | -19 |
| βzzz | 495 | 340 | 4832 | 2403 | 4305 | 2887 |
| βX | 7 | 5 | -166 | -79 | 3 | 57 |
| βY | 21 | 0 | -120 | -34 | -71 | -219 |
| βZ | 827 | 552 | 6388 | 3028 | 6789 | 4063 |
| βtot | 827 | 552 | 6391 | 3029 | 6789 | 4069 |
| βvec | 496 | 331 | 4808 | 1818 | 4074 | 2442 |
| *η*c | 0.480 | 0.63 | 0.328 | 0.34 | 0.641 | 0.44 |
| βvec */* βtot | 0.60 | 0.60 | 0.75 | 0.60 | 0.60 | 0.60 |

a Conversion factors for *β*tot from a.u. to SI and esu units: 1 a. u. =8.639418x10-33 esu

bGen. is a split basis set consisting of LAN2DZ for Iodine atom

c *η* is the ratio between off-diagonal (βyyz) and diagonal (βzzz) components

**4. Conclusions**

Hence the current research study highlights numerous insights into structure-property relationship of above entitled three novel borane-iodine compounds **1-3**. The TD-DFT calculations show that 1-nitro-4-propynyl-benzene and 1-amino-4-propynyl-benzene at top terminal positions of the parent compound lead to (92 and 35 nm) red shift and (106 and 33 nm) blue shift for maximum absorption and emission wavelengths as in compounds **2** and **3**,respectively. Likewise, FMOs study reveals the comprehensive intra-molecular charge transfer from HOMO to LUMO. The smaller electron injection energy barrier (0.75 eV) of **2** as compared to the other compounds reveal that it would be better n-channel contestant. Though the smaller hole injection energy barrier of compound **3** as compared to the other counterpartsshowed that aforementioned derivative might be better as p-channel. The calculation of second-order NLO polarizabilities (*β*tot) shows that compounds **2** and **3** possess the *β*tot amplitudes of 3029 and 4069 a. u., respectively, with CAM-B3LYP method which are reasonably larger than similar prototype molecules. The NLO anisotropies are 0.63, 0.34 and 0.44 for compound **1-3**, respectively, at CAM-B3LYP level of theory revealed that the charge transfer process in not unidirectional because of the V-shape of studied molecular systems. Thus, the NLO amplitudes and NLO anisotropies indicate that the above-entitled compounds might have significant potential to use them in NLO applications. Our quantum chemical exploration of the structural, electro-optical and nonlinear optical properties demonstrates that these materials with trustworthy properties of interests might be prospective competitors for the electro-optical device as well as NLO applications.

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1.  corresponding Authors, Tel.: +966 17 623 8450

   e-mail addresses: [archaudhry@ub.edu.sa](mailto:archaudhry@kku.edu.sa) (Aijaz Rasool Chaudhry) [↑](#footnote-ref-1)