

Electronic, Non-Linear Optical, Optoelectronic and Thermodynamic properties of undoped and doped bis (ethlenedithio) tetraselenafulvalene (BETS) (C₁₀H₈S₄Se₄)molecule: first study using ab-initio investigation

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Electronic, Non-Linear Optical, Optoelectronic and Thermodynamic properties of undoped and doped bis (ethlenedithio) tetraselenafulvalene (BETS) (C₁₀H₈S₄Se₄) molecule: first study using ab-initio investigation

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Abstract

We have performed the ab-initio calculation of the undoped and doped molecules bis (ethlenedithio) tetraselenafulvalene (BETS). Carbone (C) atoms have been substituted by Boron (B) to investigate their effects on the electronic structure, nonlinear optical, optoelectronic and thermodynamic properties of BEST molecule. The RHF and hybrid density functional theories (wB97XD, B3PW91 and B3LYP) methods were applied, using the cc-pVDZ basis set. We found that the energy gap E_{gap} of the doped molecules are respectively 2.476 eV and 2.569 eV for $\text{C}_8\text{B}_2\text{H}_8\text{S}_4\text{Se}_4$ and $\text{C}_7\text{B}_3\text{H}_8\text{S}_4\text{Se}_4$ with B3LYP/cc-pVDZ basis set, lower than one of the undoped molecule (3.316 eV). The significant increase values of polarizability ($\langle\alpha\rangle$) and first order hyperpolarizability (β) of the doped compounds, especially in $\text{C}_8\text{B}_2\text{H}_8\text{S}_4\text{Se}_4$ ($\langle\alpha\rangle = 4.5315 \times 10^{-23}$ esu, $\beta = 22672.27 \times 10^{-33}$ esu and $\langle\alpha\rangle = 4.518 \times 10^{-23}$ esu, $\beta = 23657.43 \times 10^{-33}$ esu respectively for B3LYP and B3PW91) compared to those of the undoped molecule ($\langle\alpha\rangle = 4.3602 \times 10^{-23}$ esu, $\beta = 1290.38 \times 10^{-33}$ esu and $\langle\alpha\rangle = 4.518 \times 10^{-23}$ esu) show that the new molecules have a good nonlinear optical property. Results suggest that these molecules doped with boron are a potential candidate as semiconductors compounds and nonlinear optical materials.

Keywords: ab-initio calculation, BETS, doping, electric properties, optoelectronic properties, hyperpolarizability.

1. INTRODUCTION

Since the discovery of the first organic semiconductor in 1954 [1], much theoretically and experimentally research have been carried out in the field of chemistry and physics of organic semiconductors, which gave rise to the birth of a new generation of electronic devices. Organic molecules, which are Organic optoelectronic materials attract attention for the elaboration of low-cost multi-function devices such as photovoltaic cells, thin-film transistors, light-emitting diodes (LEDs), sensors optical memories etc. [2]. One of the must study organics molecules is the bis (ethlenedithio) tetraselenafulvalene (BETS), which is a π -electron donor obtained by a modification of DEBT-TTF and by substituting selenium for sulfur in the central tetrathiafulvalene fragment [3,4]. The synthesis of the BEST was first reported by Schumaker et al [5], with CSe or H₂Se as the starting material. Some other synthesis has been proposed by Kato and al [6]. Molecule review reveals that the BETS molecule is used to build the very well know new superconductor which exhibits a diversity of physical and structural properties [7]. Ko-ichi Hiraki and al [8] performed NMR measurements to detect the π spin polarizability of the organic molecule BETS (BETS = Bis (ethylenedithio)tetraselenafulvalene) of the superconducting induced field, λ -(BETS)₂Fe_{1-x}GaxCl₄, which showed a superconducting transition at relatively low magnetic field compared to undoped λ -(BETS)₂FeCl₄. Crystal structure and electronic properties of BEST compounds with tetrahedral anions, MX₄ was examined by Kobayashi and al [9]. Although many types research have been done on the BEST compounds, many other studies can still be carried out.

The ab-initio and the density functional theory methods have proven their effectiveness in studying the structural, optoelectronic and nonlinear properties of compounds in many themes [10,11]. Our previous works on the development of new NLO materials have shown the influence of doping on the physicochemical properties of molecules [12]. So, in this work, the method cited will be used to carry out the effect of doping with boron on the bis (ethlenedithio) tetraselenafulvalene (BETS) in the ground state and design a new organic semiconductor. The geometric parameters of the BETS molecule were initially investigated. Secondly, the electronic and nonlinear properties of the undoped and doped compounds were predicted. Finally, the thermodynamic properties of the different compounds were presented.

2. METHODOLOGY AND THEORETICAL BACKGROUND

2.1. Methodology

The entire set of calculations procedure was performed using the Gaussian 09 [13] software package and an affordable full-featured graphic user interface Gauss view 6.0.16 [14] for structure modelling and visualization. Restricted Hartree-Fock (RHF) and density Function Theory with three functionals (wB97XD, B3PW91 and B3LYP) were used to predict geometrical parameters, electronic properties, thermodynamics properties of the undoped and doped molecules. The polarized valence double zeta (cc-pVDZ) basis set was applied. All the studies were carried out in the gas phase and the geometry optimization was performed in the ground state.

Initially, the structure data file (SDF/MOL File) of the BETS molecule was downloaded to the <https://www.molinstincts.com> site. The other compounds were designed and modelled to the optimization of their geometry by using Gauss View 6.0.16. After, the RHF method was used to perform the geometry optimization. Ultimately, the structure was refined using different levels of Density Function Theory which is a cost-effective method for the inclusion of electron correlation and has proven to be one of the most accurate methods for computation of the electronic structure of solid [15,16]. To evaluate the physical properties of compounds, some mathematical formulas obtainable in the literature will be used.

2.2. Theoretical background

The polarizability α is a very important parameter in understanding the optoelectronic properties of organic materials. In a dielectric material, it allows a dipole moment μ to appear under the influence of the electric field E .

In the nonlinear domain, i.e. for a strong electric field, we have:

$$\mu = \alpha E + \beta E^2 + \gamma E^3 + \dots \quad (1)$$

Where β and γ are respectively the first and second order hyperpolarizability, and represent the nonlinear response of the molecule.

The average value of dipole moment is given by

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

In the linear domain, i.e. for a weak electric field, $\beta \approx 0$ and $\gamma \approx 0$, the dipole moment is written:

$$\mu = \alpha E \quad (3)$$

The polarizability tensor components for a molecule whose represent the ease of a system to deform under the action of an electric field are given by α_{xx} , α_{xy} , α_{yy} , α_{xz} , α_{yz} and α_{zz} . These are used to calculate average polarizability α and anisotropy $\Delta\alpha$ defined by:

$$\alpha = \frac{1}{3}(\langle\alpha_{xx}\rangle + \langle\alpha_{yy}\rangle + \langle\alpha_{zz}\rangle) \quad (4)$$

$$\Delta\alpha = \frac{1}{\sqrt{2}}\left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} + \alpha_{zz})^2 + (\alpha_{zz} + \alpha_{xx})^2 + 6(\alpha_{xz}^2 + \alpha_{xy}^2 + \alpha_{yz}^2)\right]^{\frac{1}{2}} \quad (5)$$

The first molecular hyperpolarizability, β , of the molecules are calculated from the components β_{xxx} , β_{xxy} , β_{xyy} , β_{yyy} , β_{xyz} , β_{yyz} , β_{xzz} , β_{yzz} , and β_{zzz} of the hyperpolarizability using the following formulas:

$$\beta = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{xxy} + \beta_{yyy} + \beta_{yzz})^2 + (\beta_{zxx} + \beta_{zyy} + \beta_{zzz})^2\right]^{\frac{1}{2}} \quad (6)$$

The energy gap E_{gap} is an important electronic parameter to give an idea for the potential applications of our materials as semiconductors. It was calculated as follows

$$E_{\text{gap}} = E_{LUMO} - E_{HOMO} \quad (7)$$

In order to predict the global reactivity descriptors of the compounds, the ionization potential, IP, and the electronic affinity, EA, were deduced to E_{HOMO} and E_{LUMO} :

$$IP = -E_{HOMO} \quad (8)$$

$$EA = -E_{LUMO} \quad (9)$$

The electric displacement field can be obtained by the equation:

$$D = \varepsilon_0 E + P = \varepsilon_0 \varepsilon_r E = \varepsilon_0(1 + \chi_e) \quad (10)$$

Where E is the external electric field, ε_0 and ε_r the permittivity of the vacuum and the relative permittivity of the medium respectively. P is the induced electric polarization given by:

$$P = \varepsilon_0 \chi_e E = (\varepsilon_r - 1)\varepsilon_0 E \quad (11)$$

Where χ_e is the electric susceptibility defined by a formula $\chi_e = \varepsilon_r - 1$.

The refractive index is obtained by the relation,

$$\eta = \sqrt{1 + \chi_e} \quad (12)$$

The above relationships have been obtained through different papers [17-19]

electronegativity ϕ , chemical potential μ_c , global hardness M , softness ζ and Electrophilicity index ω are given by the equations [20-22].

$$\phi = -\frac{E_{LUMO}+E_{HOMO}}{2} \quad (13)$$

$$\mu_c = \frac{E_{LUMO}+E_{HOMO}}{2} \quad (14)$$

$$M = \frac{E_{LUMO}+E_{HOMO}}{2} \quad (15)$$

$$\zeta = \frac{1}{\eta} \quad (16)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (17)$$

3. RESULTS AND DISCUSSIONS

3.1 Optimized structures

The optimized molecular structures of BEST (a) and his substituted compounds (b) and (c) are presented in **figure 1**. The computed bond parameters and some experimental values observed in the literature [4] of bis (ethlenedithio) tetraselenafulvalene molecule are recorded in **table 2**.



Figure 1: Optimized geometric structure of (1a) **BETS molecule**, 3B-doped (1b) and 2B-doped (1c) to boron with B3LYP/cc-pVDZ.

In table 1, we recorded the values of the total electronic energies of the three studied molecules obtained using RHF/cc-pVDZ, wB97XD /cc-pVDZ, B3PW91/cc-pVDZ and B3LYP/cc-pVDZ level of theory. It is observed that the calculated electronic energies of all compounds are negative at all levels of theory. This means that both undoped and doped molecules are stable given the negative electronic energy. Moreover, the most stable molecules are those obtained by using B3LYP/ because of their smaller values of electronic energy. It is also observed that the values of electronic energy of doped molecules are high than the one of BETS molecule, this can be explained by the number of electrons in their structure which decreases with doping.

Table 1: Total electronic energies (E in a.u) for the optimized molecules

MOLECULE	RHF	B3PW91	WB97XD	B3LYP
C₁₀H₈S₄Se₄	-11572.617043	-11584.487416	-11584.806589	-11584.885643
C₈B₂H₈S₄Se₄	-11545.123796	-11556.812609	-11557.132593	-11557.212552
C₇B₃H₈S₄Se₄	-11531.390038	-11542.984787	-11543.306193	-11543.385549

a.u (atomic energy unit)

3.2 Geometrical parameters (Bond lengths) of BEST molecule

Table 2: Optimized bond length of bis (ethlenedithio) tetraselenafulvalene, calculated at RHF, wB97XD, B3PW91 and B3LYP level of theory methods using cc-pVDZ basis set in gas phase at 298.150K

Molecule Parameters	C ₁₀ H ₈ S ₄ Se ₄				
	RHF	wB97XD	B3PW91	B3LYP	Exp [4]
R(1,10)	1.9138	1.9108	1.9111	1.9266	1.901
R(1,11)	1.9194	1.9118	1.9159	1.931	1.922
R(2,10)	1.913	1.9098	1.9099	1.9254	1.898
R(2,14)	1.9144	1.9091	1.9138	1.9287	1.923
R(3,9)	1.9138	1.9108	1.9111	1.9266	1.916
R(3,13)	1.9194	1.9118	1.9159	1.931	1.905
R(4,9)	1.913	1.9098	1.9099	1.9254	1.896
R(4,12)	1.9144	1.9091	1.9138	1.9287	1.906
R(5,11)	1.7736	1.7621	1.7577	1.7694	1.752
R(5,15)	1.828	1.8484	1.8535	1.8674	1.809

R(6,14)	1.7734	1.7629	1.759	1.7701	1.752
R(6,16)	1.8175	1.8303	1.836	1.8478	1.805
R(7,13)	1.7736	1.7621	1.7577	1.7694	1.745
R(7,17)	1.8281	1.8484	1.8535	1.8674	1.818
R(8,12)	1.7733	1.7629	1.759	1.7701	1.745
R(8,18)	1.8175	1.8303	1.836	1.8478	1.814
R(9,10)	1.329	1.3454	1.3513	1.3505	1.338
R(11,14)	1.326	1.3458	1.3523	1.3515	1.328
R(12,13)	1.326	1.3458	1.3523	1.3515	1.338
R(15,16)	1.5199	1.5174	1.5142	1.5194	1.502
R(15,25)	1.0908	1.1009	1.1025	1.1024	-
R(15,26)	1.0874	1.0986	1.0995	1.0993	-
R(16,23)	1.0904	1.1	1.1014	1.1014	-
R(16,24)	1.0887	1.0992	1.0998	1.0996	-
R(17,18)	1.5199	1.5174	1.5142	1.5194	1.440
R(17,21)	1.0908	1.1009	1.1025	1.1024	-
R(17,22)	1.0874	1.0986	1.0995	1.0993	-
R(18,19)	1.0904	1.1	1.1014	1.1014	-
R(18,20)	1.0887	1.0992	1.0998	1.0996	-

For clarity, we present in table 2 only the optimized values of bond lengths of the undoped molecule (a) obtained after calculation, and the experimental results obtained in the literature. These optimized values were obtained using the ab-initio (RHF) and DFT (wB97XD, B3PW91 and B3LYP) methods with a cc-pVDZ basis set in the ground state. It can be observed in these results that, the values of the geometric parameter vary slightly when we move from RHF to DFT (wB97XD, B3PW91 and B3LYP) methods. The same observation can be done when we look at the results obtained by density functional theory calculation. Observing the values in table 2, we conclude that the calculated bond length values in the current work are in good agreement with the experimental one obtained by T. Courcet and al. [4].

3.3 Nonlinear optical properties of the compounds

The nonlinear optical (NLO) phenomena have attracted much attention in recent years because of their potential applications in optical communication, optical signal processing and transmission, optical data acquisition and storage, and optical computing [23]. The Extensive number of works have been performed to investigate the NLO properties of novel NLO compounds [24]. Many efforts have been made in the search for factors that can considerably

improve the first hyperpolarizability and lead to the design of new types of NLO materials [25]. the search for new functional materials through design based on chemical substitution is an emerging strategy; that can be extended to the discovery of nonlinear optical semiconductor (NLO) materials [26]. To understand the Nonlinear Optical properties of coumarin dyes, Muttannavar et al. computed dipole moment (μ), electronic polarizability (α), and the first hyperpolarizability (β) using B3LYP/6-31G(d, p) density functional theory; The results indicate that given the same number and type of atoms and double bonds in a molecule, linear conjugation excels over cyclic or crossed conjugation in enhancing hyperpolarizabilities [27]. Pimento et al. have studied methyl orange molecules under their acidic and alkaline structures and showed the inclusion of additional hydrogen changes drastically the electronic structure of the material and its NLO properties [28].

In this section, the components value of dipole moment, polarization and first hyperpolarizability are reported in table 3. These values are obtained using the output field after calculation with the gaussian 09 program.

Table 3: Components values of dipole moment μ (Debye), polarizability $\langle\alpha\rangle$ and hyperpolarizability β obtained with gaussian 09.

Molecules Parameters	C ₁₀ H ₈ S ₄ Se ₄				C ₈ B ₂ H ₈ S ₄ Se ₄				C ₇ B ₃ H ₈ S ₄ Se ₄			
	RHF	wB97XD	B3PW91	B3LYP	RHF	wB97XD	B3PW91	B3LYP	RHF	wB97XD	B3PW91	B3LYP
μ_x	-0.0000233	-0,0000135	-0.0000159	-0.0000061	0.9294424	1.3247153	1.5559658	1.5204428	-0.52777630	-0.7530892	-0.8732059	-0.8593325
μ_y	-0.0000930	0.0000040	0.0000035	0,0000009	-0.0010648	-0.0053360	-0.0070053	-0.0028510	-0.06868016	-0.0958931	-0.1248820	-0.1119074
μ_z	-0.2027701	0.6881354	0.6634181	0.6155223	-0.1759610	0.3434028	0.3935266	0.3716484	0.175137906	0.3113832	0.3677194	0.3576554
α_{xx}	415.07214	453.64185	481.70193	486.42976	435.39362	477.13727	510.36162	513.82440	444.486188	482.58853	517.02343	520.53665
α_{xy}	-0.7659336	-1.5653461	-1.8013296	-1.7457402	-0.2113927	-0.3149874	-0.3310127	-0.3379749	-1.00742849	-0.7449168	-1.4295486	-1.2756289
α_{yy}	245.75132	250.01548	254.89091	256.25012	249.27394	256.96830	262.42281	263.26781	248.150172	258.04427	263.72391	264.34400
α_{xz}	0.0115999	0.0004078	0.0006040	0.0002700	9.6366341	16.728893	19.710529	19.064201	-10.8469162	-13.641330	-15.132422	-14.876812
α_{yz}	0.0012663	0.0000690	0.0000662	0.0000268	-1.2192718	-0.5936602	-0.4503357	-0.5168794	-0.14152436	-0.3943847	-0.7114043	-0.5920215
α_{zz}	131.57216	138.05898	140.95515	139.96093	129.41660	137.43608	141.79516	140.20680	127.602174	138.18697	142.71990	140.56887
β_{xxx}	-0.0976949	-0.0115456	-0.0255528	-0.0105145	-679.61122	-1335.0137	-2465.9212	-2363.5233	455.639473	795.37327	1480.1035	1436.5102
β_{xxy}	0.0447303	0.0018936	0.0056693	0.0020878	-0.2086735	-2.4885095	-26.257442	-27.662219	21.4050074	94.028589	195.40271	184.00007
β_{xyy}	0.0667337	0.0057707	0.0066024	0.0027832	-90.618409	-142.89589	-176.95896	-173.02465	42.1419619	78.318952	86.429711	87.607215
β_{yyy}	0.0051889	-0.0005997	0.0001791	-0.0000988	-0.9038383	-1.2794823	-5.7749679	-5.5540721	19.0197531	41.042270	49.945455	49.448991
β_{zxx}	-28.429471	46.327743	92.619271	84.414786	-201.32032	-325.13902	-583.07843	-550.36034	-212.045838	-438.54938	-766.25596	-718.59138
β_{xyz}	-16.721579	-36.359152	-34.863380	-34.258082	-8.9662645	-18.923401	-20.503193	-19.708786	9.14363559	27.308957	48.978451	45.087503
β_{zyy}	21.621635	30.070311	40.557825	39.159409	-1.7941550	-13.491464	-13.190374	-13.380849	-20.7999042	-44.124391	-50.910082	-49.802802
β_{yzz}	0.0050428	0.0005016	0.0006141	0.0003035	-48.094965	-85.383300	-177.00426	-156.12404	36.7371896	79.552776	145.76550	131.34777
β_{zzz}	0.0069831	-0.0014957	-0.0026814	-0.0010650	3.0894410	-1.5520594	-3.9050846	-3.9008093	-2.38055264	5.1313783	10.982444	8.7303541

β_{zzz}	-22.492355	29.795398	27.772030	25.787437	-45.793052	-42.527273	-74.102371	-66.591185	-4.29317978	-35.953860	-74.506426	-61.725679
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The dipole moment μ , average polarizability $\langle\alpha\rangle$, anisotropy $\Delta\alpha$ and first hyperpolarizability β of the molecules are calculated using the formulas (2), (4), (5) and (6).

Table 4 resumes all the calculated values for the undoped and doped molecules in all levels of theory.

Table 4: calculated values of dipole moment μ (Debye), average polarizability $\langle\alpha\rangle * 10^{-24}$ (e.s.u), anisotropy $\Delta\alpha * 10^{-24}$ (e.s.u) and first hyperpolarizability $\beta * 10^{-33}$ (e.s.u) of $C_{10}H_8S_4Se_4$, $C_7B_3H_8S_4Se_4$ and $C_8B_2H_8S_4Se_4$

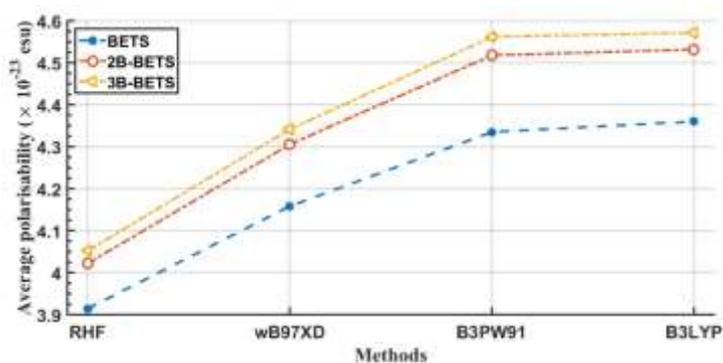
Molecules Parameter s	$C_{10}H_8S_4Se_4$				$C_7B_3H_8S_4Se_4$				$C_8B_2H_8S_4Se_4$			
	RHF	wB97XD	B3PW91	B3LYP	RHF	wB97XD	B3PW91	B3LYP	RHF	wB97XD	B3PW91	B3LYP
μ (Debye)	0.5154	1.7491	1.6862	1.5645	1.4242	2.0857	2.4290	2.3829	2.4044	3.4784	4.0795	3.9784
$\langle\alpha\rangle * 10^{-23}$ (esu)	3.9144	4.1581	4.3351	4.3602	4.052	4.3414	4.5619	4.5717	4.0216	4.3054	4.518	4.5315
$\Delta\alpha * 10^{-23}$ (esu)	2.5891	2.9042	3.1486	3.2006	2.9098	3.183	3.4779	3.5279	2.8039	3.1424	3.4295	3.4732
$\beta * 10^{-33}$ (esu)	253.13	917.44	1390.48	1290.38	4791.58	9008.80	16015.60	15386.20	6980.64	13221.33	23657.43	22672.27

Figure 2 shows us the different variations of the characteristic properties of nonlinear optics. By observing the curves of figure 2, we make a remark that the values vary according to the methods of use, the functional ones and the doping.

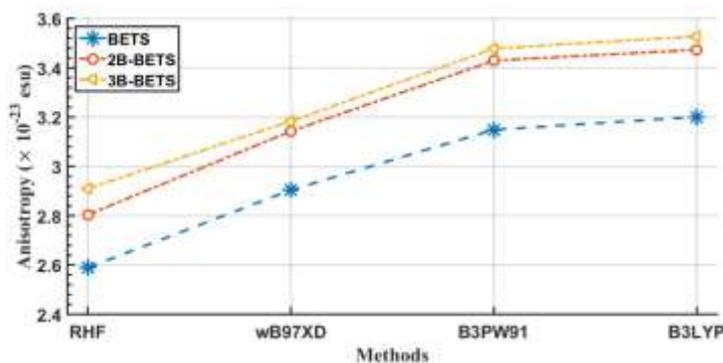
The curves of the graph (2a) and (2b) represent respectively the variations of the values of the polarizability and the anisotropy. For the undoped molecule (BETS), these values vary slightly when we pass from the uncorrelated method to the correlated methods; this is the effect of electronic correlation. For the doped compounds (2B-BETS and 3B-BETS), in addition to the effect of the correlation induced by the application of the DFT, the substitution of the carbon atoms by the boron atoms leads to an improvement of these properties as observed in the two graphs (2a) and (2b) of figure 2. In addition, the proportion of boron atoms slightly influences these values; this is best appreciated in Table 4.

Determining the hyperpolarizability of a molecule is very useful for understanding the relationship between molecular structure, but also nonlinear optical properties. The curves of

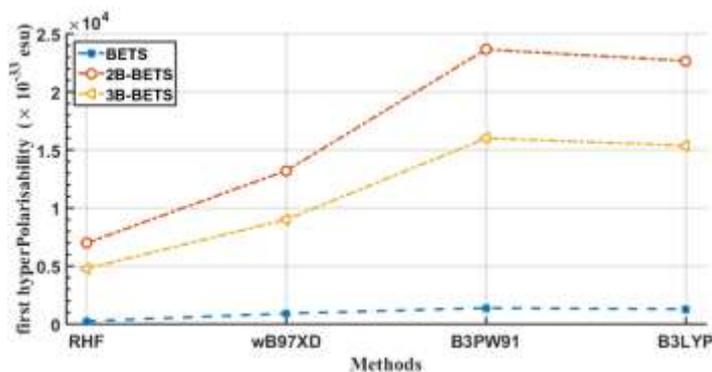
the graph (2c) represent the variations of the values of the first-order hyperpolarizability for the different molecules. We note that these values increase according to the electronic correlation whether the molecule is doped or not. But also, we notice that for the RHF method, the values of the first-order hyperpolarizability increase when we pass from the undoped molecule to the doped molecules. With the consideration of the electronic correlation by application of the DFT functionals, we observe a very large increase in these values. According to the literature, there are two values of the first-order hyperpolarizability β which serve as a reference for NLO materials; namely that of urea (928×10^{-33} esu) [29, 30] and that of para-Nitroaniline (pNA) (1072 ± 44 a.u. = 9261×10^{-33} esu) [31]. By comparing the values β in table 4 with those of the various literary references, it emerges that the values obtained for the functionals B3LYP and B3PW91 are at least twice as large. We can say that the substitution of carbon by boron atoms on the BETS molecule has made it possible to considerably increase its nonlinear character; But also, that the number of boron atoms in the structure reduces the value β . Both functionals B3LYP and B3PW91 are those giving a better appreciation of this nonlinear character. Moreover, based on the values of the electronic and gap energy (E_{gap}) obtained from Tables 1 and 5, we can say that the most suitable function for this study is B3LYP.



(2a)



(2b)



(2c)

Figure 2: Average polarizabilities, anisotropies and First molecular hyperpolarizabilities of the molecules of bis (ethlenedithio) tetraselenafulvalene and their derivatives 3B and 2B substituted $C_{10}H_8S_4Se_4$ with **RHF/cc-pVDZ**, **wB97XD/cc-pVDZ**, **B3PW91/cc-pVDZ** and **B3LYP/cc-pVDZ** methods

3.4 Electronic properties and chemical descriptors

The frontier molecular orbitals of a compound are at the frontier of electron occupation. The HOMO and LUMO are types of molecular orbitals which means the highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively. HOMO has low energy, electrons tend to hold in this molecular orbitals and is viewed as nucleophilic; while LUMO has a very high energy, thus contains no electrons and it is electrophilic in the ground state.

Figure 3 show us the different LUMO and HOMO orbitals of our studied compounds. It is observe that the charge transfer on LUMO-HOMO orbitals is the same for uncorrelated methods to DFT methods (figure 3a). for figure 3b and 3c, we observed dans the charge transfer on the LUMO-HOMO orbitals are totally different; this means that the substitution of carbo with boron element have a strongly impact in the charge distribution of the compounds.

– LUMO and HUMO diagram

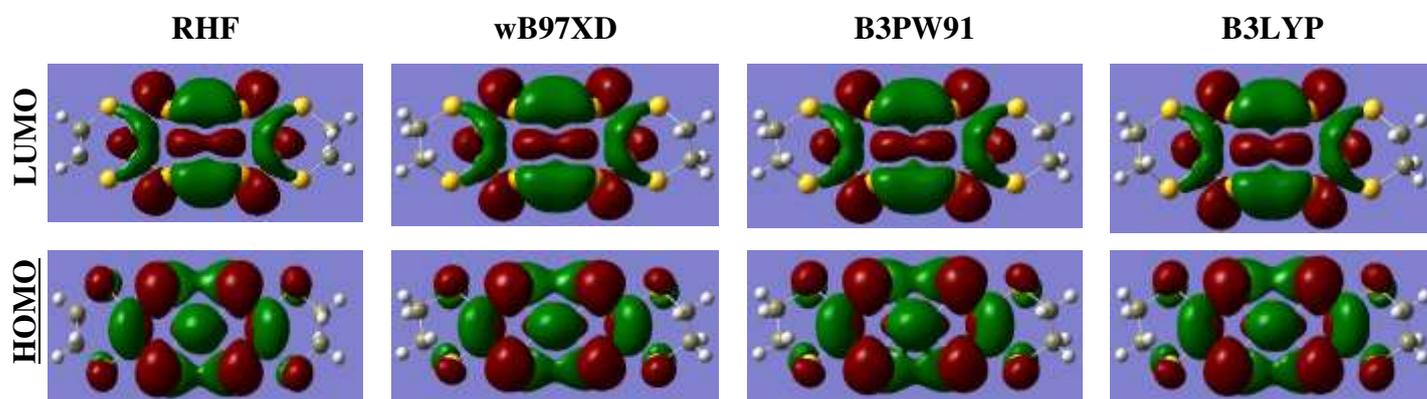
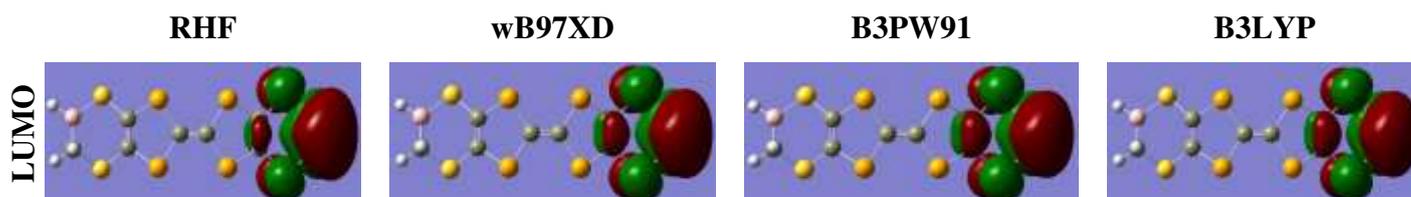


Figure 3a: LUMO and HOMO molecular orbital diagram of the undoped studied molecular structure obtained using cc-PVDZ Basis set.



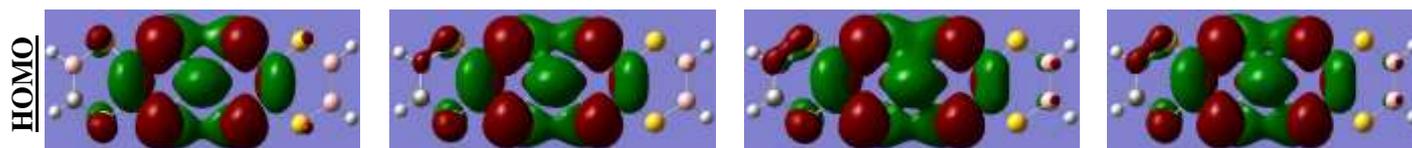


Figure 3b: LUMO and HOMO molecular orbital diagram of the 3B doped studied molecular structure obtained using cc-PVDZ Basis set.

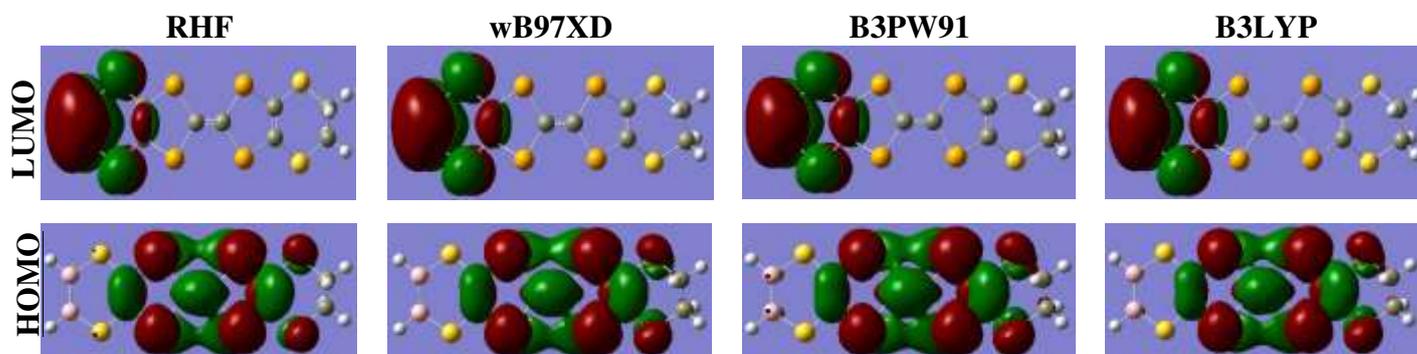
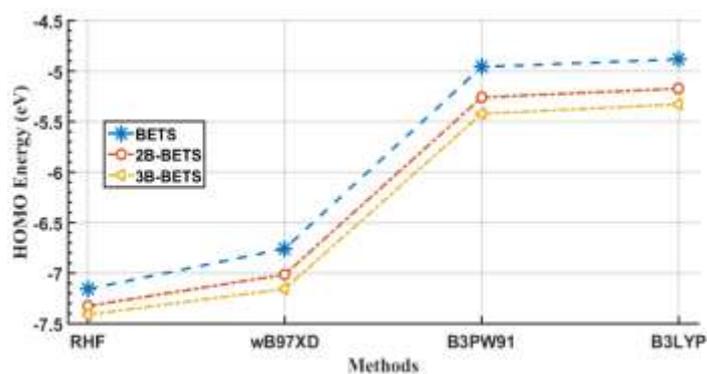


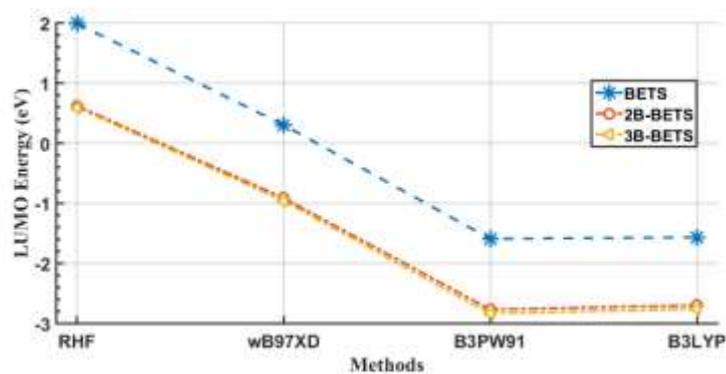
Figure 3c: LUMO and HOMO molecular orbital diagram of the 2B doped studied molecular structure obtained using cc-PVDZ Basis set.

Figure 3: LUMO and HOMO molecular orbital diagram of the BETS (3a), 3B-BETS (3b) and 2B-BETS(3c) studied molecular structure obtained using cc-PVDZ Basis set

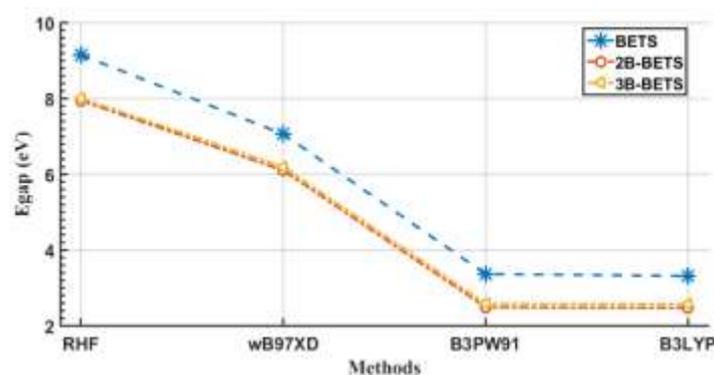
The values of the HOMO and LUMO energies are contained in table 5. The values of the HOMO show an increase in these energies for each molecule when we pass from the uncorrelated method to the correlated method. But also, the HOMO energies decrease from the undoped molecule to the doped molecules. This is illustrated by the graph (4a) in Figure 4. For LUMO energies, the values decrease from the uncorrelated method to the correlated methods. Likewise, they decrease from the undoped molecule to the doped molecules. This is illustrated by graph (4b) in Figure 4. We can conclude that doping with boron had the effect of increasing the nucleophilicity and decreasing the electrophilicity of the molecule.



(4a)



(4b)



(4c)

Figure 4: HOMO Energy (E_{HOMO}), LUMO Energy (E_{LUMO}) ionization potential and energy gap (E_{gap}) of the molecules of bis (ethlenedithio) tetraselenafulvalene and their derivatives 3B and 2B substituted $\text{C}_{10}\text{H}_8\text{S}_4\text{Se}_4$ with RHF/cc-pVDZ, wB97XD /cc-pVDZB3LYP, B3PW91/cc-pVDZ and B3LYP/cc-pVDZ methods

The difference between the HOMO and LUMO energies is the energy gap (E_{gap}). It is an important parameter used to understand the reactivity and stability behavior of the compound. The calculated values of the energy gap are recorded in table 5. We observe in the graph (4c) in figure 4 that the values of energy gap are different from RHF method to the DFT Methods and decreased from the undoped to doped compounds. We also observe that the number of Boron substitution element changed the gap energy. The best values E_{gap} obtained for our calculation are for B3LYP functional and respectively 2.476 eV, 2.569 eV for $\text{C}_8\text{B}_2\text{H}_8\text{S}_4\text{Se}_4$ and $\text{C}_7\text{B}_3\text{H}_8\text{S}_4\text{Se}_4$. Because the energy gap of semiconductors is between 1 to 3 eV [32], according to the band theory, we deduce that both compounds are good semiconductors at the correlated method using B3LYP functional. We also notice that the values of E_{gap} given by B3PW91 functional are less than 3 eV, which means that our compounds are good semiconductors at the level of theory. To compare the E_{gap} values of the doped compounds with those of the

electrochemically and optically obtained in literature [33] (range of 2.08-2.77 eV), we observe that our result lies with range. For the uncorrelated method RHF and correlated method wB97XD, the calculated values of gap E_{gap} of both compounds are greater than 4 eV, we deduce that our compounds are an insulator [34]. We can conclude from the above that B3LYP and B3PW91 are the appropriate level of theory to study this doped molecule. But the indicated one is B3LYP because their E_{gap} values are better estimated and their total electronic energy is smaller than the other one. This estimation is clearly visible in the table 5 and table 1.

Table 5 : Evaluation of the energy E_{HOMO} , E_{LUMO} , E_{gap} , ionization potential IP , electron affinity EA , electronegativity ϕ , chemical potential μ_c , global hardness M , softness ζ and Electrophilicity index ω values of the molecules of **bis (ethlenedithio) tetraselenafulvalene**, 3B and 2B substituted $\text{C}_{10}\text{H}_8\text{S}_4\text{Se}_4$ with **RHF/cc-pVDZ**, **wB97XD /cc-pVDZ**, **B3PW91/cc-pVDZ** and **B3LYP/cc-pVDZ** methods

Molecules Parameters	$\text{C}_{10}\text{H}_8\text{S}_4\text{Se}_4$				$\text{C}_7\text{B}_3\text{H}_8\text{S}_4\text{Se}_4$				$\text{C}_8\text{B}_2\text{H}_8\text{S}_4\text{Se}_4$			
	RHF	wB97X D	B3PW9 1	B3LYP	RHF	wB97X D	B3PW9 1	B3LYP	RHF	wB97X D	B3PW91	B3LYP
E_{HOMO} (eV)	-7,157	-6,758	-4,958	-4,883	-7,412	-7,156	-5,422	-5,328	-7,325	-7,014	-5,260	-5,173
E_{LUMO} (eV)	1,993	0,303	-1,593	-1,567	0,594	-0,962	-2,834	-2,759	0,624	-0,912	-2,769	-2,697
E_{gap} (eV)	9.150	7.062	3.365	3.316	8.006	6.194	2.587	2.569	7.950	6.102	2.491	2.476
IP	7.157	6.758	4.958	4.883	7.412	7.156	5.422	5.328	7.325	7.014	5.260	5.173
EA	-1.993	-0.303	1.593	1.567	-0.594	0.962	2.834	2.759	-0.624	0.912	2.769	2.697
ϕ	2,581	3,227	3,275	3,224	3,409	4,059	4,128	4,044	3,350	3,963	4,014	3,935
μ_c	-2,581	-3,227	-3,275	-3,224	-3,409	-4,059	-4,128	-4,044	-3,350	-3,963	-4,014	-3,935
M	4,575	3,530	1,682	1,658	4,003	3,096	1,293	1,284	3,974	3,050	1,245	1,238
ζ	0,218	0,283	0,594	0,603	0,249	0,322	0,772	0,778	0,251	0,327	0,802	0,807
ω	0,728	1,475	3,188	3,136	1,451	2,660	6,586	6,365	1,411	2,574	6,470	6,254

The values of ionization potential (IP) and electron affinity (EA) are calculated and recorded in table 5. There are the absolute value of HOMO and LUMO energies, respectively. We observe that IP decreases from uncorrelated method to correlated methods for each molecule and increases from undoped to doped molecules; while EA increases from RHF to DFT methods and from undoped ($\text{C}_{10}\text{H}_8\text{S}_4\text{Se}_4$) to doped ($\text{C}_7\text{B}_3\text{H}_8\text{S}_4\text{Se}_4$ and $\text{C}_8\text{B}_2\text{H}_8\text{S}_4\text{Se}_4$) molecules. Large are the values of IP and EA, highest are the stability of compound. For the observation about IP and EA of our molecule, we conclude that the doped compounds are more stable than the undoped one.

3.5 Optoelectronic properties

The optoelectronic properties such as Electric field (E), Polarization density (P), Electric displacement field (D), Electrical susceptibility (χ_e), dielectric constant (ϵ_r), Dielectric constant (ϵ) and refractive index (η) of the molecule in the gas phase were evaluated using ab-initio and DFT methods (B3LYP/ **cc-pVDZ** and B3PW91/ **cc-pVDZ**) are given in table 6.

From table 6, we found that the electric field, polarization density and electric displacement increase when moving from RHF to DFT methods and for the undoped to doped molecules. Moreover, we observe that for the doped molecules, this increase is at least 50% when we move from the compound **C₈B₂H₈S₄Se₄** to the compound **C₇B₃H₈S₄Se₄**, compared to the compound **C₁₀H₈S₄Se₄**. The electrical susceptibility, dielectric constant and refractive index vary very slightly from one method to another and according to the doping. The refractive indices of the various compounds obtained after calculation are higher than those of certain reference materials in optoelectronics such as glasses whose refractive index is equal to 1.5 [35].

Table 6: Electric field (E), Polarization density (P), Electric displacement field (D), Electric susceptibility (χ_e), relative dielectric constant (ϵ_r), dielectric constant (ϵ) and refractive index (η) of **bis (ethlenedithio) tetraselenafulvalene**, 3B and 2B substituted **C₁₀H₈S₄Se₄**.

Molecules Parameters	C₁₀H₈S₄Se₄				C₇B₃H₈S₄Se₄				C₈B₂H₈S₄Se₄			
	RHF	wB97XD	B3PW91	B3LYP	RHF	wB97XD	B3PW91	B3LYP	RHF	wB97XD	B3PW91	B3LYP
E(V.m⁻¹) x10⁹	0.397	1.269	1.173	1.082	1.060	1.449	1.606	1.572	1.803	2.437	2.724	2.648
P (C.m⁻²) x10⁻³	8.775	36.466	28.414	29.425	27.36	37.602	44.256	51.647	55.136	71.725	65.330	82.943
D (V.m⁻¹) x10⁻²	1.229	4.770	3.880	3.901	3.675	5.043	5.850	6.557	7.110	9.330	8.944	10.639
χ_e	2.495	3.245	2.734	3.070	2.915	2.930	3.111	3.709	3.452	3.323	2.708	3.536
ϵ_r	3.495	4.245	3.734	4.070	3.915	3.930	4.111	4.709	4.452	4.323	3.709	4.537
ϵ x10⁻¹¹	3.094	3.759	3.307	3.604	3.466	3.480	3.640	4.170	3.942	3.828	3.283	4.017
η	1.869	2.060	1.932	2.017	1.978	1.982	2.028	2.170	2.110	2.079	1.926	2.130
R x10⁻¹⁰ (m)	5.82	5.44	5.84	5.63	5.59	5.71	5.69	5.37	5.27	5.46	5.94	5.44

3.6 Thermodynamic properties

Table 7 resumes the average values of thermodynamic properties of bis (ethlenedithio) tetraselenafulvalene (BETS) which is an undoped molecule and its doped compounds (3B and 2B). these values were calculated in the gas phase, applying the normal conditions of

temperature (298.150 Kelvin) and pressure (1 Atm). The values such as Zero Vibrational Point Energy (ZPVE), Gibbs free energy (G), Thermal Energy (E), Entropy (S), Enthalpy (H) and molar heat Capacity at Constant Volume (Cv) of the different molecules are recorded in table 3. We observe for each of these three compounds a slight variation in **E**, **H**, **G**, **Cv** and **S** when we start from the uncorrelated (RHF) to correlated (wB97XD, B3PW1, B3LYP) level of approximation and also in different correlated methods. For the undoped molecule, the values of ZPVE, **E**, **H** and **G** decreases slightly while the **Cv** and **S** increase at the level of theory. In the same way, by looking at the variation of the thermodynamic properties of the doped molecules, the same observations are made for ZPVE and **E_{thermal}**, **Cv** and **S**, from the RHF to correlated methods. The observations made above for each of the molecules prove that the electronic correlation has an impact on their thermodynamic properties.

All the values of the energies contained in table 7 were obtained by applying self-consistent field which describes the stability of the compound. By generally observing the thermodynamic properties of doped molecules, we find that the values of energies such as **H**, **G**, **Cv** and **S** are greater than those of the undoped molecule, which mean the molecule are stable. Similarly, the ZPVE and **E_{thermal}** is smaller than those of the undoped molecule. This shows that, although the effect electronic correlation makes it possible to better appreciate these properties, the doping by boron also considerably affect the thermodynamic properties. Our results also show that the calculated enthalpy and Gibbs free energy in the studied molecules are all negative, so these molecules are thermodynamically stable.

Table 7 : Zero Vibrational Point Energy (ZPVE), Gibbs free energy (G), Thermal Energy (E), Entropy (S), Enthalpy (H), molar heat Capacity at Constant Volume (Cv) of the molecules Obtained using **RHF/cc-pVDZ**, **wB97XD/cc-pVDZ**, **B3PW91/cc-pVDZ** and **B3LYP/cc-pVDZ** methods at constant temperature (T=298.1500 K) and pressure (P=1.0000 atm).

Molecules Parameters	C ₁₀ H ₈ S ₄ Se ₄				C ₇ B ₃ H ₈ S ₄ Se ₄				C ₈ B ₂ H ₈ S ₄ Se ₄			
	RHF	wB97XD	B3PW91	B3LYP	RHF	wB97XD	B3PW91	B3LYP	RHF	wB97XD	B3PW91	B3LYP
ZPVE(Kcal.mol⁻¹)	104.492	98.404	96.880	96.140	73.718	69.705	68.710	68.160	84.341	79.615	78.416	77.801
H (a.u)	-11572.430	-11584.628	-11584.311	-11584.710	-11531.252	-11543.173	-11542.853	-11543.255	-11544.968	-11556.984	-11556.666	-11557.067
G (a.u)	-11572.504	-11584.703	-11584.387	-11584.787	-11531.325	-11543.248	-11542.929	-11543.330	-11545.043	-11557.059	-11556.741	-11557.142
E_{thermal} (Kcal.mol⁻¹)	116.828	111.226	109.907	109.292	86.076	82.528	81.684	81.219	96.660	92.388	91.348	90.837

C_v (cal.mol ⁻¹ . k ⁻¹)	68.28 4	71.168	72.208	72.845	69.05 1	71.531	72.366	72.847	68.56 0	71.136	72.048	72.590
S (cal.mol ⁻¹ . k ⁻¹)	156.9 97	158.408	159.938	161.10 5	154.5 28	157.791	158.323	159.03 0	155.7 43	157.894	158.635	159.57 7

4. CONCLUSION

In this work, Restricted Hartree-Fock (RHF) and density functional theory (DFT) have been carried out to study the nonlinear optical, electronic, optoelectronic and thermodynamic properties of undoped and doped BETS molecules. The main idea of the research was to show the impact of doping on the initial BETS compound. Firstly, we observe that for all levels of theory, undoped molecules or original compounds present weak NLO properties. Secondly, we found that boron doping systematically influences some properties when we compare it to the initial compound. The values of the first hyperpolarizability of the doped molecule are highest than the one of undoped BETS molecule and above the reference values of NLO materials in the literature. The values of the gap energy of doped compounds range between **2,476** and **2.587** eV, less than 3 eV. We deduce from what preceding that these new materials can find their application in NLO and are semiconductor materials that can be used in optoelectronic devices of communication, electronics, Light Transmitting Diode (LED), photonics materials and field effect-transistor (FET). Finally, in view of the thermodynamic properties, we can say that our new compounds are stable.

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Author contribution statement

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Data availability

All data generated or analyzed during this study are included in this published article

Declaration of Competing Interest

The authors declare no conflict of interest.

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