Eng. Sci., 2022, **19**, 319–329

Engineered Science

DOI: https://dx.doi.org/10.30919/es8d714

Density Functional Theory Studies on a Novel 1-Ethyl-4-phenyl-1,5-benzodiazepin-2-thione molecule and its derivatives for Opto-nonlinear applications

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Abstract

Herein, we have studied a new 1,5-benzodiazepin derivative named 1-Ethyl-4-phenyl-1,5-benzodiazepin-2-thione] (EPBZ) and designed its several derivatives using chlorine (Cl), fluorine (F), bromine (Br), hydroxyl (OH), methyl (CH_3), methoxy (OCH_3), nitro group (NO_2), and amine (NH_2) groups and a comparative investigation has been presented. The geometries of EPBZ compound and its derivative were attained using Becke three-Lee–Yang–Parr (B3LYP) density functional theory (DFT) with 6-31G** and the results indicated their stability. Absorption spectra possess only one absorption peak(s) at ~ 260 nm attributed to π to π* transition in the ultraviolet (UV) region for all molecules. However, the highest-occupied molecular orbital (HOMO) in EPBZ and its derivative products occurs in one of benzene rings and the substituents, the reverse happens in the case of the lowest-unoccupied molecular orbital (LUMO). The antibonding π* in LUMO and its next orbital of HOMO-LUMO are usually confined in two benzene rings which prolong over the entire molecule. In the case of derivatives, the HOMO–LUMO gap lies within 3.38 and 4.01 eV, which is comparatively lower than the primary EPBZ. EPBZ and its derivatives possess higher β_{tot} values compared to urea, though the largest value of β_{tot} is noticed for EPBZ-NH_2 derivative compared to all which is ~ 2060 times higher than that of urea. EPBZ-NH_2 derivative β_{tot} value is very high which suggests its use in nonlinear optical (NLO) applications.

Keywords: Organic molecules; Density functional theory; Molecular modeling; Optical properties; Nonlinear optic.
Received: 19 February 2022; Revised: 16 May 2022; Accepted: 16 May 2022.
Article type: Research article.

1. Introduction

The nonlinear optical (NLO) properties of the materials arising from the atomic/molecular interactions with intense electric fields like laser have been attracting a great deal of research attention from both the theoretical and experimental community owing to their enormous applications in materials science and engineering, and various spectroscopic fields.[1] In addition, the theoretical modeling[2-9] has a great role in the designing of pioneering NLO compounds by providing vital information regarding the structural properties and relationships pertaining to the molecular engineering of the materials of interest.[10-12] Also, there is a number of inorganic molecules that are used and suggested for various applications.[13-17] NLO properties are observed in both organic and inorganic compounds. However, based on their nature, they have found diverse applications in various fields. In particular, organic crystals are observed to be possessing better NLO characteristics compared to their inorganic counterparts. Although the stability of inorganic compounds is comparatively better their amplitudes of the first hyperpolarizability are mostly observed to be poor. Moreover, organic NLO compounds' superior confrontation towards laser mutilation and higher first and second

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hyperpolarizabilities (β & γ) compared to the inorganic compounds make them a better choice for applications in a hefty simple harmonic generation. Also, the higher β values due to charge transmission happening intra-molecularly through the extended π-conjugated electron array from the donors to the acceptors set of organic conjugated molecules significantly favor NLO properties. In addition, organic materials also have the advantage of structural diversity with low cost and easy fabrication procedures.

The present work aims a detailed analysis of various substitutions in bicyclic heterocyclic 1,5-Benzodiazepines compound wherein a benzene ring fused to a seven-membered ring of diazepine and adopts a boat conformation holding two nitrogen atoms at the first and fifth positions of the later ring. These rings are aromatic in nature and are inclined at 34.7° compared to each other. 1,5-Benzodiazepine derivatives belong to the important classes of heterocyclic molecules having significant applications in medicinal chemistry. They are extensively used as drugs, pharmaceuticals, anti-microbial,[18,19] anticonvulsant,[20] anti-HIV-1,[21] and antitumor agents.[22] They are also utilized in the growth of varieties of heterocyclic compounds as intermediates.[23,24] They also found uses in therapeutics against cardiovascular disorders and viral infections.[25] They can also actively engage to counter the effects of potassium blockers and peptide hormones.[26]

The theoretical calculations in this study are focused on the detailed analysis of the effects of various substitutions in 1, 5-Benzodiazepine [1-Ethyl-4-phenyl-1,5-benzodiazepin-2-thione] (EPBZ) using time-dependent DFT (TDDFT) for the first time. As DFT has been found to be one of the best computation studies for various types of molecules.[27-30] The substitutions are Cl (EPBZ-Cl), F (EPBZ-F), Br (EPBZ-Br), OH (EPBZ-OH), CH_3 (EPBZ-CH_3), OCH_3 (EPBZ-OCH_3), NO_2 (EPBZ-NO_2) and NH_2 (EPBZ-NH_2) at the position X in EPBZ as displayed in Fig. 1 below.

2. Computational details

In the present study, all calculations of the molecular geometry structure of EPBZ and its derivatives were performed using the Gaussian 09 program. Also, the theoretical calculations were done on the gaseous phase with the assumption of the isolated molecules, using the GaussView-05 program. The geometries were optimized by employing the B3LYP functional combining Becke's 3 nonlocal hybrid exchange potential parameters[31] and the nonlocal correlation proposed by Lee, Yang, and Parr,[32] using the 6-31++G** basis sets, which is a gateway methodology in contemporary computational approach in chemistry. The calculations on frequencies were made at the same level of theoretical assumptions and no negative frequencies were detected. The nonexistence of imaginary frequencies indicates the global minima of the structure in the study for the potential energy hypersurface. The molecular structure of the reference compound is shown in Fig. 1. The structure was optimized to use in the calculation of Infrared and vibrational (IR and Raman) frequencies. The IR and Raman spectra of EPBZ and its derivatives were accomplished from the second derivative of the energies, by means of analytical computation to identify any imaginary frequency. Excitation spectra of EPBZ and its derivative molecules were computed in the gaseous phase using TDDFT[33-35]), at the same theoretical level.

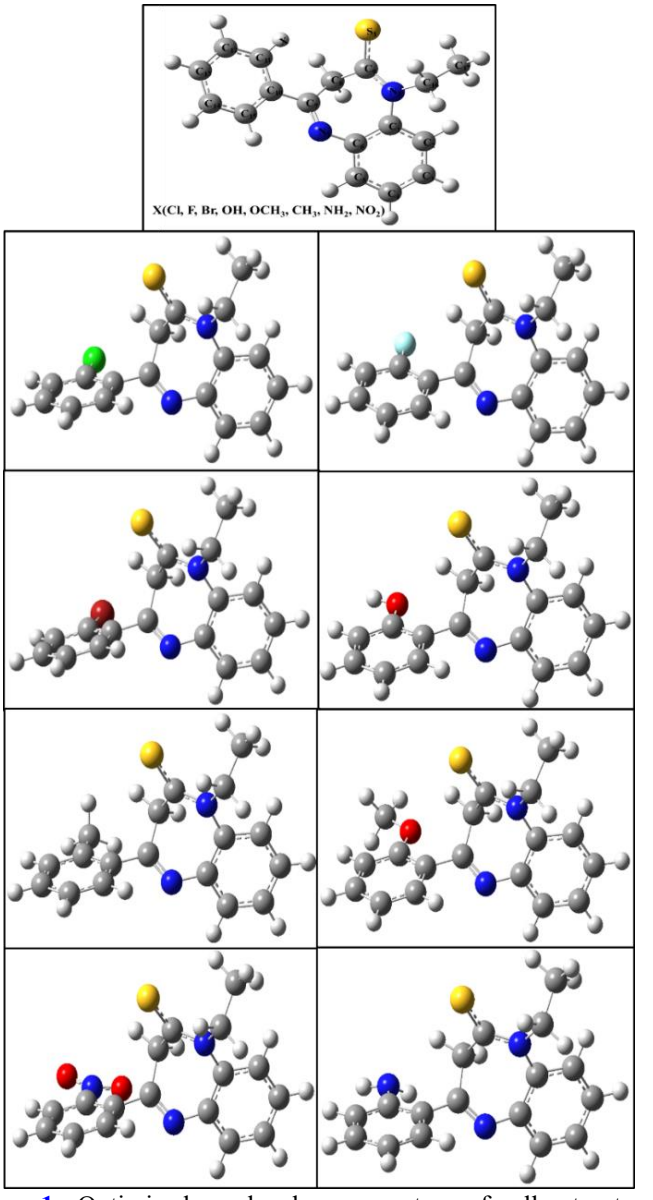

Fig. 1 Optimized molecular geometry of all structures corresponding at EPBZ and its derivatives.

In a similar manner, a finite field (FF) theoretical approach using 6-31++G** level was followed to calculate the values and components of the total static first hyperpolarizability (β_{tot}). This is now an established methodology on varieties of molecules-organic/inorganic/semi-organic types offering steady outcomes in the computational values of the first hyperpolarizability.

In this formalism, the energy (E) of the molecule upon exposure to a static electric field (F) is computed based on the formula:

$$E = E^{(0)} - \mu_1 F_1 - \frac{1}{2}\alpha_{ij}F_iF_j - \frac{1}{6}\beta_{ijk}F_iF_jF_k - \frac{1}{24}\gamma_{ijkl}F_iF_jF_kF_l \quad (1)$$

here, $E^{(0)}$ represents to total energy of the molecule in absenteeism of electronic fields, vector components of dipole moment(μ), linear(α), second and third-order polarizabilities, *etc.* The μ, α, β, and γ are the proportionality terms in Eq. (1), and hence differential of E w.r.t. F can yield the respective values of μ, α and 1st hyperpolarizability (β). Herein, we have computed μ, α, and β values.

Total dipole moment (μ_{tot}) is defined as follows:

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

Isotropic polarizability $\alpha_{(0)}$ as:

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

Anisotropy of polarizability ($\Delta\alpha$) is:

$$\Delta\alpha = \frac{1}{\sqrt{2}}\sqrt{[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}{}^2]} \quad (4)$$

Similarly, the static first hyperpolarizability values are obtained from:

$$\beta_{tot} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \quad (5)$$

$$\beta^{vec} = \frac{3}{5}\beta_{tot} \quad (6)$$

where β_x, β_y and β_z are computed following:

$$\beta_x = (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})$$
$$\beta_y = (\beta_{yyy} + \beta_{xxy} + \beta_{yyz})$$
$$\beta_z = (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})$$

Hence, $\beta_{tot} = \sqrt{[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yyz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})]^2}$ (7)

Though the static 1st hyperpolarizability has to be represented by 27 component third rank tensor illustrated by a 3×3×3 matrix, the Kleinman symmetry makes it easy to identify or reduce the number of the component using the symmetry rule $\beta_{yxy} = \beta_{yyx} = \beta_{yyz} = \beta_{yzy} = \beta_{zyy}$, *etc.*, and thus the 27 components of the matrix could be represented by 10 components (as shown in Table S1).[36]

3. Results and discussion

3.1 Optimization of molecular geometry

Stable optimized geometries of EPBZ and its derivatives attained from the B3LYP/6-31++G** scheme are depicted in Fig. 1. The results of the geometric parameters for the different substitutions have been included in the supplementary material. As per Table S1 (see supporting information) the geometries obtained computationally are close to the experimental data.[37] The aromatic ring with the substituents rotates 90 degrees with respect to the rest of the compound, and this is due to the steric effect of the substituents. Inside, all the substitutes transformed systematically within the same ring link to attain the most diverse analogs set. The tabulated data in Table 1 clearly shows the closeness of computed bond lengths and angles to that of experimental parameters, which is an indication of the accuracy of the current computational result and in other words gives validation to the theoretical approach we followed. However, we observed a slight difference in bond lengths and angles of EPBZ and its derivatives between the calculated and the experimental crystal structure data, especially the computed bond length value is found to be higher than that of the experimental result in the range ~ 0.015- 0.99 Å.[38] The dihedral angles tend to remain at 0° and 180°.

3.2. UV–Visible studies

Figure 2 represents the absmpounds of EPBZ computed using the TD-B3LYP/6-31++G** scheme. As observed in the case of most of the organic compounds, here the absorption spectral peak is observed within the 200-700 nm range (as shown in Fig. 2), where the spectral peaks originated due to the π–π* transitions.

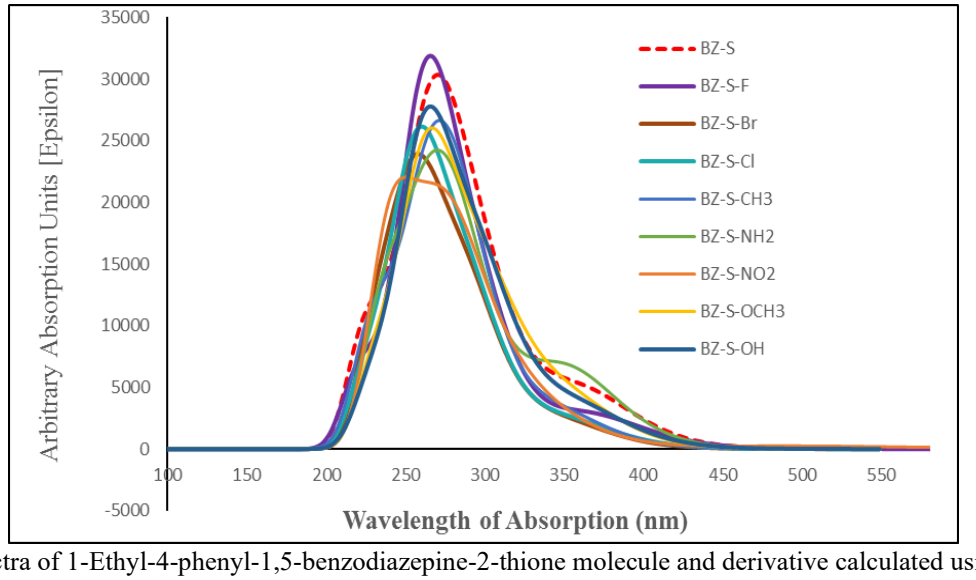

Fig. 2 UV-visible spectra of 1-Ethyl-4-phenyl-1,5-benzodiazepine-2-thione molecule and derivative calculated using the Functional and basis set (B3LYP/6-31++G**).

Table 1. Calculated energy values, their differences of frontier molecular orbitals (FMOs), and GCRD parameters of EPBZ compound and its derivatives.

Orbital energy	Energy (eV)								
Molecules	EPBZ	EPBZ- Cl	EPBZ- F	EPBZ-Br	EPBZ-OH	EPBZ-CH_3	EPBZ-O-CH_3	EPBZ-NO_2	EPBZ NH2
E_{HOMO}	-5.88	-5.83	-5.80	-5.83	-5,67	-5.79	-5.65	-5.92	-5,68
E_{HOMO-1}	-6.08	-6.14	-6.10	-6.14	-5,95	-6.07	-5.92	-6.22	-5,91
E_{LUMO}	-2.0	-1.89	-2.02	-2.86	-1,79	-1.78	-1.74	-3.04	-1,75
E_{LUMO+1}	-1.45	-1.51	-1.47	-1.51	-1,34	-1.44	-1.32	-1.85	-1,37
$\Delta E_{HOMO-LUMO}$	3.88	3.94	3.78	3.97	3.88	4.01	3.92	2.88	3.94
$\Delta E_{HOMO-1-LUMO+1}$	-4.63	-4.63	-4.63	-4.63	-4.62	-4.63	-4.61	-4.38	-4.54
Hardness (η)	1.94	1.97	1.89	1.98	1.93	2.0	1.96	1.44	1.97
Potential (μ)	-3.94	-3.86	-3.91	-3.84	-3.73	-3.78	-3.69	-4.48	-3.72
Softness (S)	0.26	0.25	0.26	0.25	0.26	0.25	0.25	0.34	0.25
Electronegativity (χ)	3.94	3.86	3.91	3.84	3.73	3.78	3.69	4.48	3.72
Electrophilic index (ω)	4.0	3.78	4.04	3.72	3.59	3.57	3.47	6.96	3.51

The time-dependent DFT method has been considered one of the powerful quantum mechanical theoretical approaches in material science to calculate the excited state electronic structure. Compared to conventional ab initio/semi-empirical techniques, the approaches based on density functional theory are contemporary and provide accuracy with computational efficiency. In the present case, we observed the spectral peak at the 260 nm range which could be attributed to the highest occupied to the lowest unoccupied molecular orbital (HOMO to LUMO) transition. The computed spectrum also illustrates a few characteristic bands accountable for the transfer of charges. The spectral peak of the substitution of the F is higher than the EPBZ molecule and the rest of the substituents remain below. This result demonstrates that EPBZ and its all derivatives can be applied for NLO applications.

3.3 Analysis of frontier molecular orbitals (FMO)

Figures 3-10 represents the computed frontier molecular orbitals of all the molecules under the study. The figure reveals the characteristic features of the valence structures of the EPBZ compound and its derivatives. These studies on the FMO are very useful in estimating the electrical and optical characteristics of organic molecules. The increase of the two orbital overlapping means the increased or stable molecular orbital bonding with a corresponding increase in the destabilization of the antibonding. The HOMO – LUMO distributions of the studied molecule and their derivatives are depicted in Fig. 3, which demonstrates the HOMO−1, HOMO, LUMO, and LUMO+1 orbitals computed using B3LYP/6-31++G** levels. The corresponding energy distribution levels are tabulated in Table 1.

This study reveals the delocalized state of HOMO in the two aromatic rings, while HOMO−1 is not located in the aromatic ring of the substituents. The study also reveals the localized orbitals of π* anti-bonding LUMO and LUMO+1 encompassing throughout the system. The energy gap among HOMO and LUMO are obtained to be nearly 3.88 eV for the parent compound offering good kinetic stability for the compound with a promising chemical hardness of 1.94 eV. However, in the case of EPBZ compound derivatives, the HOMO–LUMO gap is obtained within ~ 2.88 - 4.01 eV range.

The hardness (η), softness (S), chemical potential (μ), electrophilicity index (ω), and electronegativity (χ) evaluations are usually classified under the global chemical reactivity descriptor (GCRD) data which provide significant information regarding the chemical reactivity and stability of the molecule and are also identified as useful in quantifying the structural properties, structural analysis on activity/toxicity and in evaluating the relationship between the aromaticity and hardness.[39] Table 1 displays the calculated GCRD data of η, μ, S, χ, and ω for the EPBZ derivatives. DFT results are now established to explain the reactivity and stability.[40] We used the E_{HOMO} and E_{LUMO} as the ionization potential (I) and electron affinity (A) correspondingly for the computation of η, μ, S, χ, ω. The results very well confirm the stability of the molecules under study.

3.4. NLO studies

The calculated NLO constraints like α_0, Δα, μ, β along with their parts were obtained from B3LYP/6-31++G** methodology for EPBZ and its derivative as presented in Table S2 (provided as supplementary data). However, the main total values of α_0, Δα, μ, and β for all molecules are provided in Table 2 for better and easy comparison for unit conversion of α, 1 a.u. = 1.820×10^{-25} esu, and β, 1 a.u. = 8.629×10^{-33} esu are used. The largest value of β_{tot} was noticed for the EPBZ molecule when the NH_2 group has been added compared to all other modified as well as parent EPBZ molecules. Moreover, the β_{tot} values of all EPBZ and their derivatives are larger than the standard Urea molecule. The β_{tot} value is noticed to be 2060 times larger for EPBZ derivative modified with NH_2 group (i.e. 768.1×10^{-30} esu) than urea ($\beta_{urea} = 0.3728 \times 10^{-30}$ esu),[41-44] Though, all EPBZ derivative, as well as parent molecules, possess larger values than urea.[41-44]

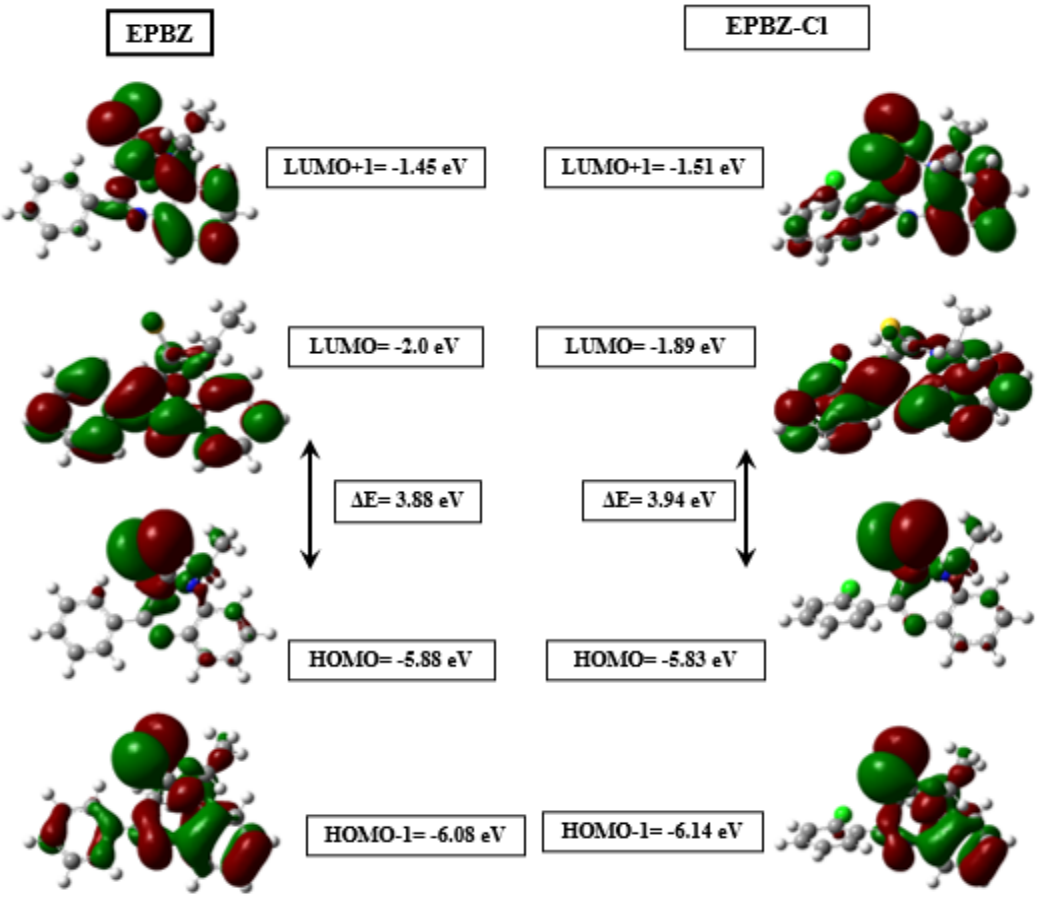

Fig. 3 HOMO-LUMO orbitals for EPBZ and its derivative molecule with Cl.

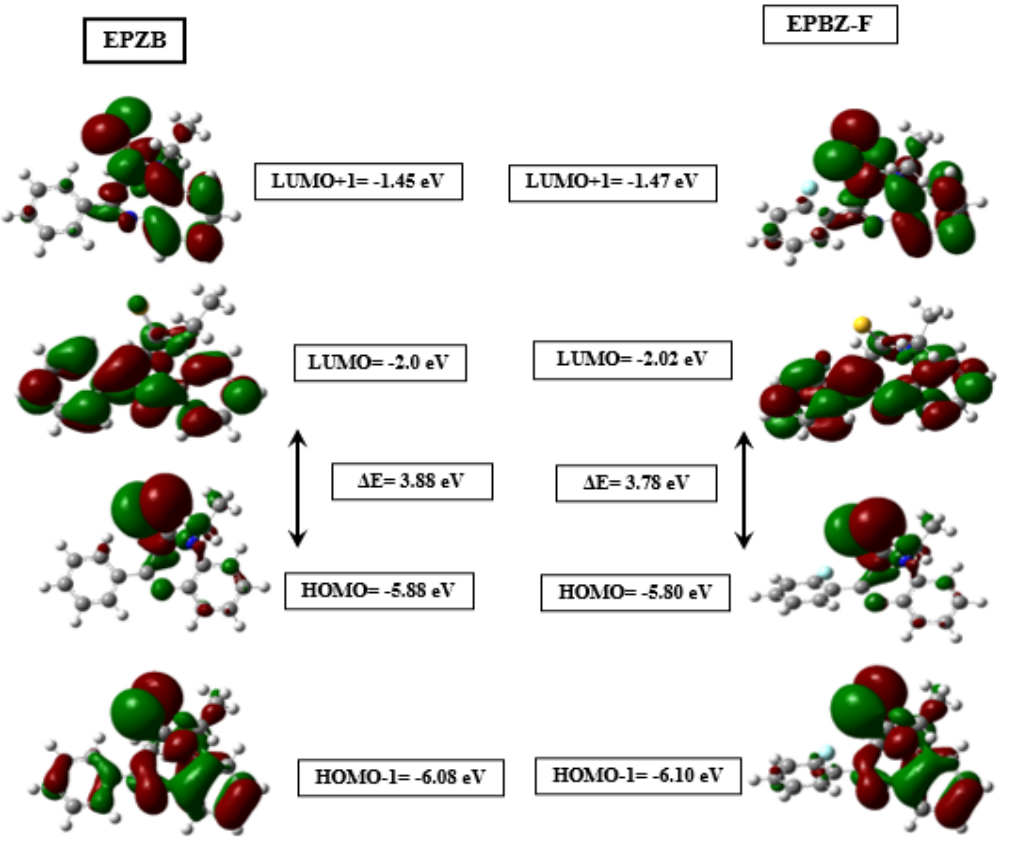

Fig. 4 HOMO-LUMO orbitals for EPBZ and its derivative molecule with F.

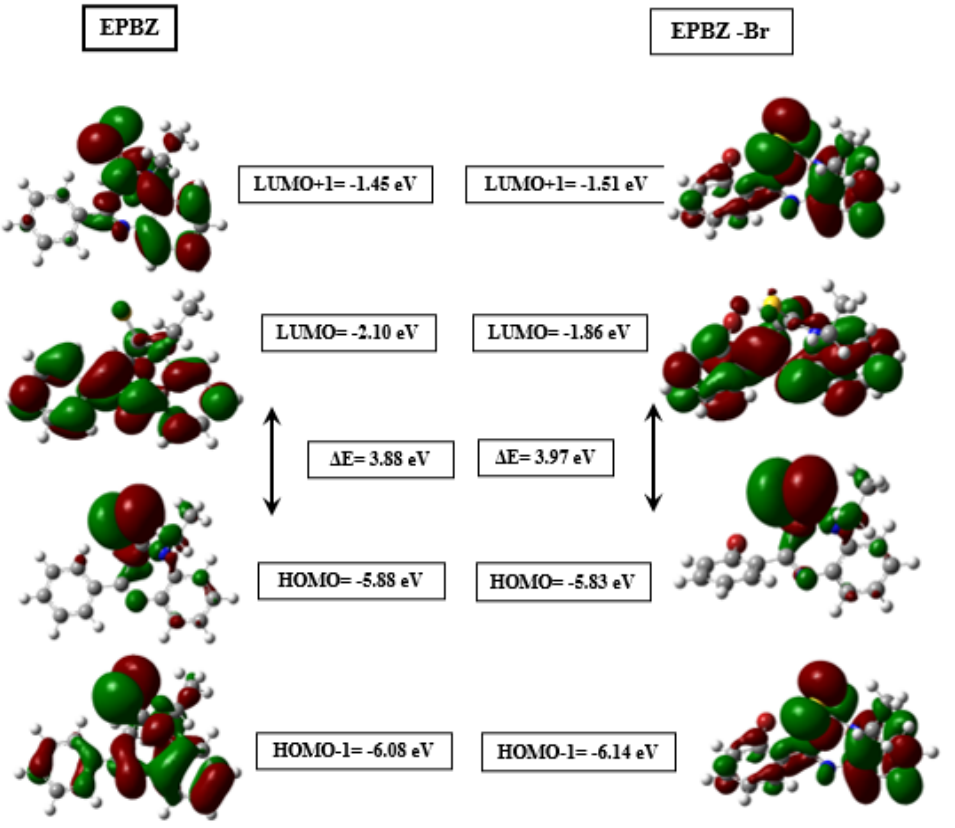

Fig. 5 HOMO-LUMO orbitals for EPBZ and its derivative molecule with Br.

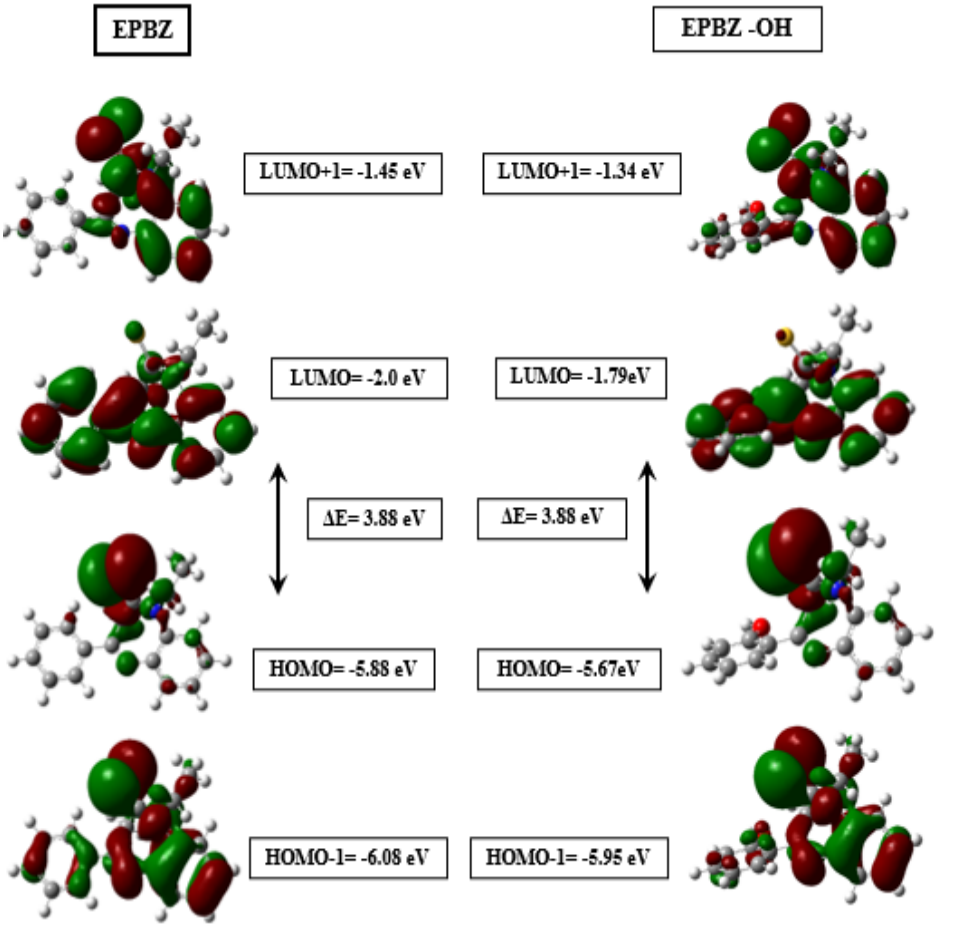

Fig. 6 HOMO-LUMO orbitals for EPBZ and its derivative molecule with OH.

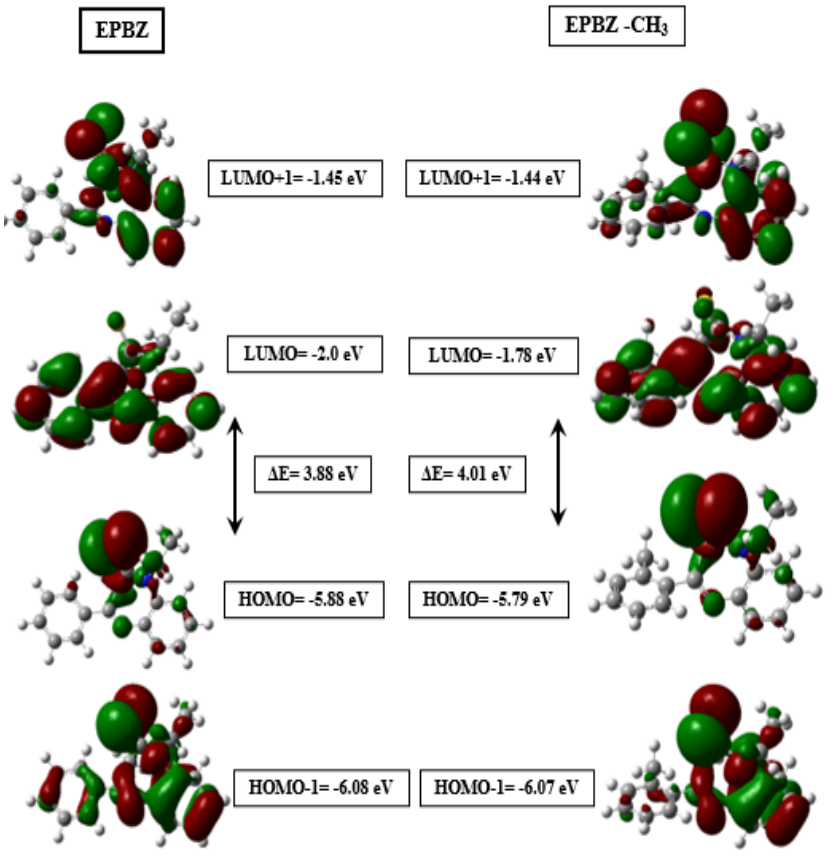

Fig. 7 HOMO-LUMO orbitals for EPBZ and its derivative molecule with CH_3.

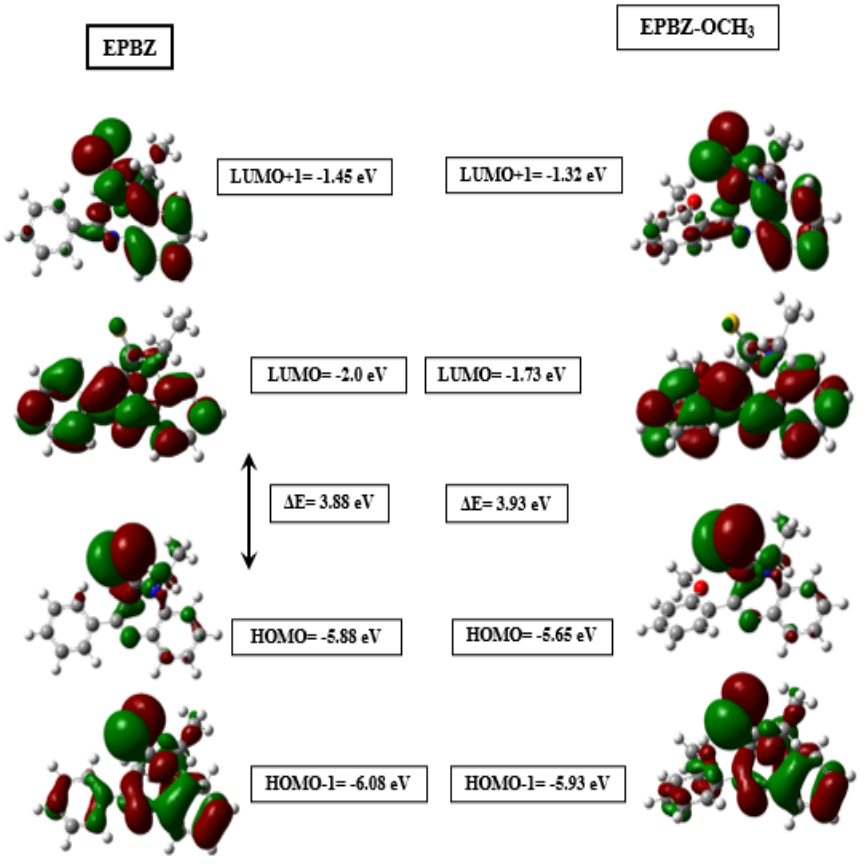

Fig. 8 HOMO-LUMO orbitals for EPBZ and its derivative molecule with OCH_3.

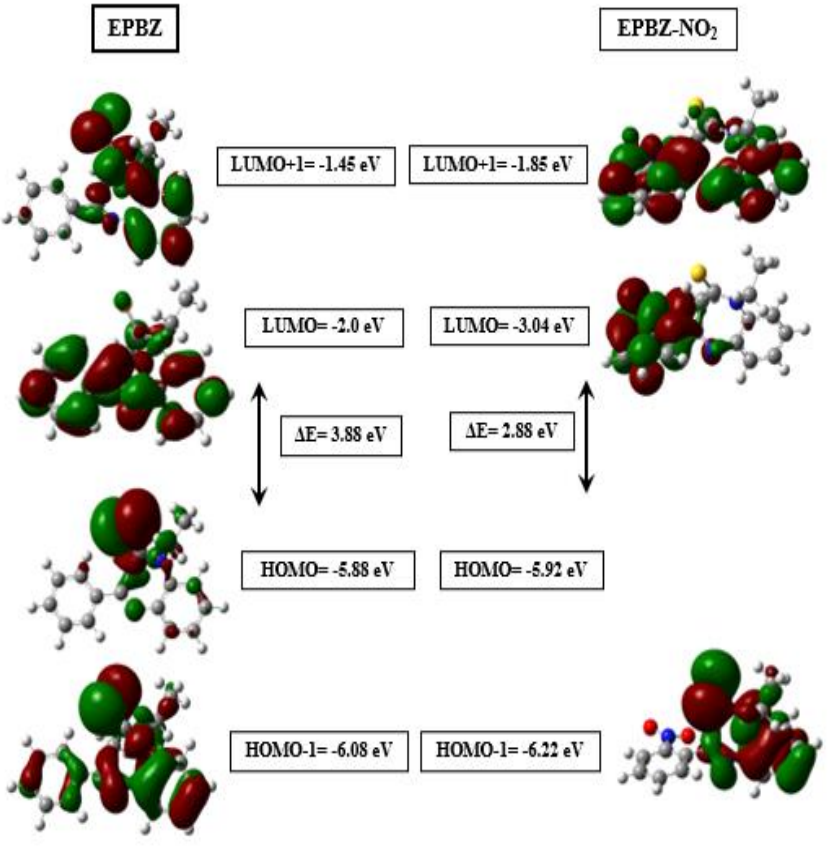

Fig. 9 HOMO-LUMO orbitals for EPBZ and its derivative molecule with NO_2.

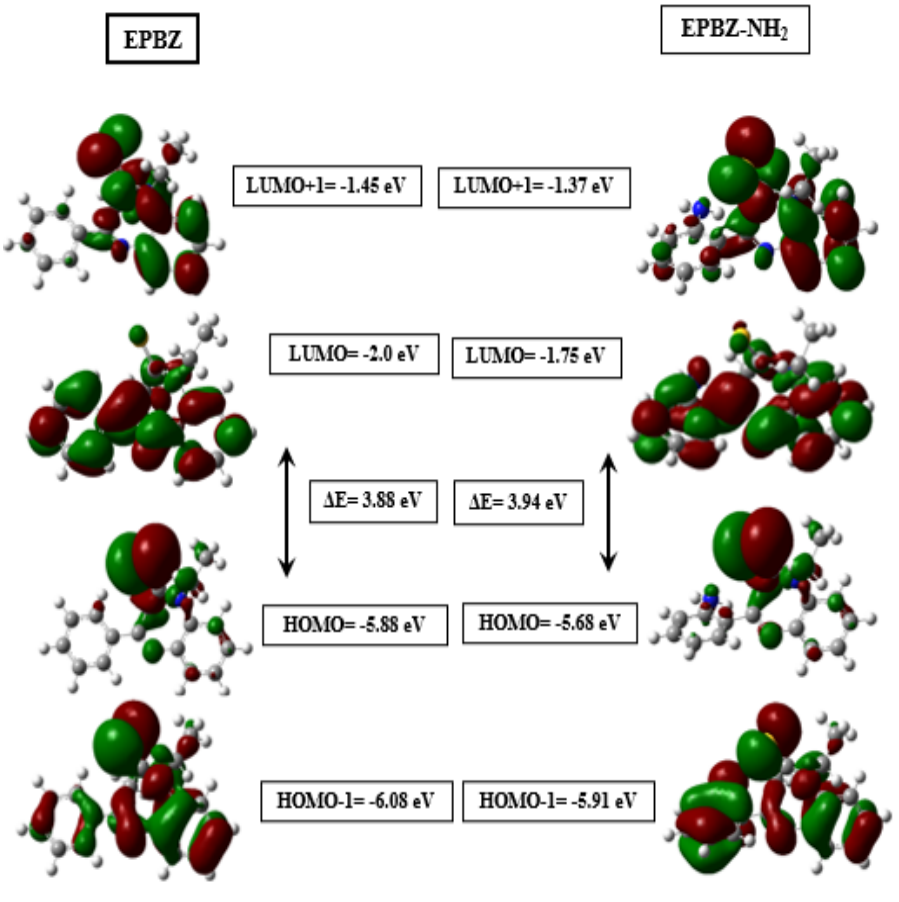

Fig. 10 HOMO-LUMO orbitals for EPBZ and its derivative molecule with NH_2.

Table 2. Polarizabilities, dipole moments, and hyperpolarizabilities values of 1-Ethyl-4-phenyl-1,5-benzodiazepine-2-thione (EPBZ) molecule and its derivatives calculated at B3LYP/6-31++G** level of theory.

Molecules	α_0 esu. ($\times10^{-24}$)	Δ_α esu. ($\times10^{-24}$)	μ_{total} D	β_{total} esu. ($\times10^{-30}$)	β_{vec} esu. ($\times10^{-30}$)
EPBZ	223.8	109.2	2,9176	321.8	193.1
EPBZ-Cl	259.2	112.3	2,9534	345.5	207.3
EPBZ-F	250.3	140.8	3.0984	433.7	260.2
EPBZ-Br	266.7	104.2	2.8898	128.9	77.3
EPBZ-OH	255.8	37.9	2.0951	528.7	4.6
EPBZ-CH_3	260.7	128.3	2.9756	339.5	203.7
EPBZ-O-CH_3	269.0	130.6	2.4242	407.4	224.4
EPBZ-NO_2	263.9	118.9	4.4744	649.2	389.5
EPBZ-NH_2	261.1	132.4	3.5922	768.1	460.9

4. Conclusion

The optimization of molecular geometry by DFT at B3LYP using 6-31G** levels for the EPBZ and its derivative molecules indicates the stability of these molecules. All the geometrical parameters were obtained within the standard limits. The absorption spectral data were evaluated using TD-B3LYP method at 6-31++G** for the EPBZ primary and its derivative molecules is used to determine the absorption spectra. The obtained results show that they have one characteristic absorption peak at ~ 260 nm in the UV range due to the π-π* transition. In HOMO-LUMO analysis, while the location of HOMO for the EPBZ and its derivative molecules appeared in one of the benzene rings and its substituent, the opposite occurred in the case of LUMO. For the LUMO and LUMO + 1 orbitals, the π* antibonding is typically confined on two-benzene rings, and this nature was found to be extended through the entire molecule. Moreover, the energy gaps amongst HOMO and LUMO for EPBZ derivative molecules are obtained in the range 2.88 - 4.01 eV, which is slightly lower than that of the primary EPBZ molecule. The computed GCRD parameters validated the chemical stabilities of all the molecules. The β_{tot} values are noticed to be larger for EPBZ and its derivatives compare to urea, however, the highest value of β_{tot} is observed for EPBZ-NH_2 derivative compared to all and about 2060 times higher than urea. The remarkable value of β_{tot} for EPBZ-NH_2 derivative signifies its importance of it in NLO applications. This value is several times higher compared to several another organic/semi-organic molecules which are reported previously.[45-49]

Acknowledgment

The authors would like to express their gratitude to the Deanship of Scientific Research at King Khalid University for funding this work through Research Groups Program under Grant No. R.G.P. 2/83/43. The calculations have been performed at GRUPO2 computer center of the Quantum Chemistry Groups of the Departamento de Química Física Aplicada, Universidad Autónoma de Madrid, Spain.

Conflict of Interest

The authors declare no conflict of interest.

Supporting information

Applicable.

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