Theoretical Investigation Of The Molecular Structure, Vibrational Spectra, Thermodynamic And Nonlinear Optical Properties Of 4',5'-dibromo-2',7'-dinitro-fluorescein

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ABSTRACT

We have theoretically studied the dipole moment μ, average polarizability ($\langle\alpha\rangle$), anisotropy ($\Delta\alpha$), first molecular hyperpolarizability (β), zero point vibrational energy (ZPVE), sum of electronic energy without zero point correction (E_{elec}), with zero-point correction (E_0), with thermal energy (E_{therm}), with enthalpies (H), with free energies (G), molar heat capacity at constant volume (C_v) and entropy (S) with cc-pVDZ basis set of 4',5'-dibromo-2',7'-dinitro-3-oxo-3H-spiro[2-benzofuran-1,9'-xanthene]-3',6'-diolate. We used the RHF and DFT (PBE1PBE, MPW1PW91, B3PW91 and B3LYP) to determine the above properties and to see the correlation effect of electrons.

INTRODUCTION

There is a wide application of dyes in versatile industries, medicinal or food activities increase [1-3] problems such as toxicity, carcinogenicity, mutagenic, teratogenic problems and hazards for some microorganisms [4, 5]. These contaminants have adverse effects on human health that preoccupy researchers in order to achieve safe and clean media [6, 7]. Dyes enter into organism's lives via pulmonary and digestive systems (water or food) [8, 9] which requires the preliminary clean up procedure before their entrance to water bodies.

OBJECTIVES

The aims of this study are to calculate the molecular structure, electric parameters and optoelectronic properties and to compare the performances of the RHF and different DFT methods with cc-pVDZ basis set .

MATERIALS AND METHODS

Methods

- RHF (Restricted Hartree-Fock)
- DFT/ PBE1PBE (The 1996 pure functional of Perdew, Burke and Ernzerhof and is known in the literature as PBE0)
- MPW1PW91 (Perdew-Wang exchange as modified by Adamo and Barone combined with PW91 correlation)
- B3LYP (Beck's exchange correction functional which is base on LDA, GGA, L, Y, P and Vosko, Wilk Nusair correlation functional)
- B3PW91 (functional with the non-local correlation provided by Perdew/Wang 91)
- Dunning's correlation consistent valence polarized double Zeta (**cc-pVDZ**) basis set were used. **Basis Sets:** Mathematical functions used to describe electron distribution.

Materials

- **Environments :** Gas (air)
- **Software:** windows version of Gaussian 09 and GaussView 05
- **Microsoft office 2013**

RESULTS AND DISCUSSIONS

- The optimized structure of the compound

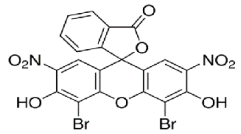


Figure 1: the structure of 4',5'-dibromo-2',7'-dinitro-3-oxo-3H-spiro[2-benzofuran-1,9'-xanthene]-3',6'-diolate

Electric parameters: Dipole moment (μ), average polarizability ($<\alpha>$), related anisotropy ($\Delta\alpha$) and first molecular hyperpolarizability.

All electric values were obtained from the output files and converted into the given units and these parameters were calculated using the following equations [10]

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \quad (1)$$

$$<\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

$$\beta = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \quad (3)$$

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

Table 1: Electric parameters of the molecules obtained at RHF, PBE1PBE, MPW1PW91, B3PW91 and B3LYP levels of theory by employing the cc-pVDZ basis set.

	Methods/ cc-pVDZ				
Parameters	RHF	PBE0	MPW1PW91	B3PW91	B3LYP
μ (*10^{-29}Cm)	1,777	1,522	1,532	1,520	1,513
$\langle\alpha\rangle$ (*10$^{-9}C^2m^2J^{-1}$)	4,33	4,96	4,95	5,03	5,06
$\Delta\alpha$(*10^{-11}esu)	1,432	2,103	2,103	2,16	2,18
β(*10^{-30}esu)	4,07	3,44	3,46	4,89	3,45

Due to the large first molecular hyperpolarizability and dipole moment of this molecule, we think that this compound has potentials applications in the field of optoelectronic. This can be a promising material for optical applications.

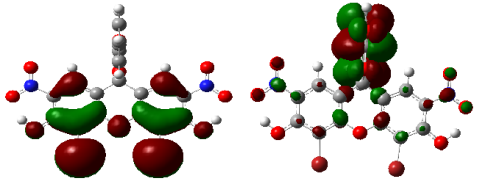
- **Thermodynamic properties and HOMO-LUMO Orbitals**

The thermodynamic properties such as the zero point vibrational energy (ZPVE), sum of electronic energy without zero point correction (E_{elec}), with zero-point correction (E_0), with thermal energy (E_{therm}), with enthalpies (H), with free energies (G), molar heat capacity at constant volume (C_v) and entropy (S) of the molecule are computed and shown in Table 2

E0 =Eelec +ZPVE (5), E= E_0 + E_{vib} + E_{rot} +E_{trans} (6), H=E+RT (7), G=H-TS (8)

Table 2: Thermodynamics Properties

	Methods/ cc-pVDZ				
PARAMETERS	RHF	PBE0	MPW1PW91	B3PW91	B3LYP
E_{elec} (a.u)	-6689,35	-6699,42	-6701,7	-6701,1	-6701,71
ZPVE (kcal/mol)	176,65	165,09	165,12	163,66	162,63
E0	-6689,07	-6699,15	-6701,43	-6700,84	-6701,45
H	-6689,04	-6699,13	-6701,41	-6700,82	-6701,42
Cv (cal/mol-K)	92,82	97,97	97,94	98,58	99,04
S (cal/mol-K)	176,53	181,61	181,51	182,22	182,81



HOMO LUMO

Figure 2: HOMO and LUMO orbitals

Radius (R), volume (V) and The optoelectronic properties such as electric field (E), polarization density (P), electric susceptibility (χ), dielectric constant (ε), refractive index (n), and the magnitude of the displacement vector (D).

Figure 3: Ionisation enrgy (EI) electron affinity (AE) and band gap energy (Egap)

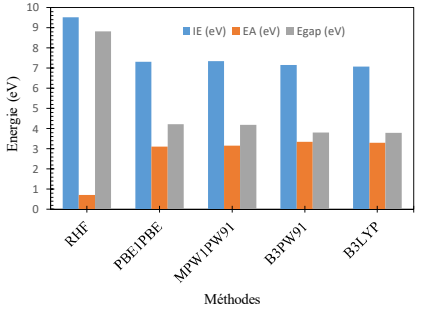


Table 3: Optoelectronic properties and energy band gap.

	Methods/ cc-pVDZ				
Parameters	RHF	PBE0	MPW1 PW91	B3PW 91	B3LYP
R (Å)	5,71	5,9	5,84	5,75	5,98
V (*10^{-28}m^3)	1,86	2,05	1,99	1,9	2,14
E(*10^{09} Vm^{-1})	4,1	3,07	3,09	3,02	2,99
P(Cm^{-2})	0,09	0,07	0,08	0,08	0,07
χ	2,63	2,73	2,81	2,99	2,67
ε(*10^{-11})	3,21	3,3	3,37	3,53	3,25
n	1,9	1,93	1,95	2	1,92
D	0,13	0,1	0,1	0,1	0,1
Egap (eV)	8,81	4,22	4,19	3,81	3,78

Figure 3 shows the variation of (EI), (AE) and (Egap) of the compound using different levels of approximation.

We can show the evolution of the electric field, polarization density and the magnitude of the displacement vector decreased when we go from RHF to PBE1PBE, MPW1PW91, B3PW91, and B3LYP by 16.64%, 33.33%, 27.27%, and 29.81%, respectively. For radius and volume, the values increase from RHF to PBE1PBE by 3.25 %, decreases by 1,04 % and by 1,50% to MPW1PW91 and B3PW91 respectively and increases by 4,03 to B3LYP. The radius, volume, electric susceptibility, dielectric constant and refractive index increased when we go from RHF to PBE1PBE, MPW1PW91, B3PW91, and B3LYP methods by 12.73%, 3.25 %, 3.56%, 2.55%, and 1.28%, respectively.

CONCLUSION AND OUTLOOK

- Its values of band gap energy (3,78-4,22 eV) in the correlated methods enables the compound to be transparent with the visible radiation and infra-red at 298,15K. Which corresponds to a threshold of absorption in the ultraviolet close relation and its small value at B3LYP shows us that this compound can be used in dye sensitizers solar cells.
- The lowest value (-6701,71 a.u) of Eelec at B3LYP shows us that the compound is most stable and the highest value (-6689,35 a.u) in RHF is less stable.
- The correlation effect of electron is observed on **figure 3** for the values of ⟨ (EI), (AE) and (Egap)
- This compound constitutes an attractive object for future studies of NLO properties, because of its higher values of the electric parameters.
- B3LYP and MPW1PW91 are well defined to produce the best results of our study.

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