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 (α), anisotropy (Δα), first molecular hyperpolarizability (β), zero point vibrational energy (ZPVE), sum of electronic energy without zero point correction (Eelec), with zero-point correction (Eelec-w), with thermal energy (Etherm), with enthalpies (H), with free energies (G), molar heat capacity at constant volume (Cv), 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 electric field.

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 prophyaxis 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-pVQZ 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 (Becke’s exchange correction functional which is base on LDA, GGA, L, Y and Yosko, Wilk Nussair correlation functional)
- B3PW91 (functional with the non-local correlation provided by Perdew Wang 91)
- Dunning’s correlation consistent valence polarized double Zeta (cc-pVQZ) basis set were used

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

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

RESULTS
- The optimized structure of the compound

Figure 2: HOMO and LUMO orbitals

Figure 3: ionisation energy (EI) electron affinity (AE)

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

<table>
<thead>
<tr>
<th>Method</th>
<th>Parameters</th>
<th>RHF</th>
<th>PBE0</th>
<th>MPW1PW91</th>
<th>B3PW91</th>
<th>B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>α (10^-18 esu)</td>
<td>4.82</td>
<td>5.00</td>
<td>5.03</td>
<td>5.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E (10^-18 esu)</td>
<td>1.49</td>
<td>2.80</td>
<td>2.91</td>
<td>2.81</td>
<td>2.81</td>
<td></td>
</tr>
</tbody>
</table>

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

Thermodynamic properties and HOMO-LUMO Orbitals

The thermodynamic properties (Eelec) as the zero point vibrational energy (ZPVE), sum of electronic energy without zero point correction (Eelec), with zero-point correction (Eelec-w), with thermal energy (Etherm), with enthalpies (H), with free energies (G), molar heat capacity at constant volume (Cv) and entropy (S) of the molecule are computed and shown in Table 2

Table 2: Thermodynamic Properties

<table>
<thead>
<tr>
<th>Method/ cc-pVDZ</th>
<th>Parameters</th>
<th>RHF</th>
<th>PBE0</th>
<th>MPW1PW91</th>
<th>B3PW91</th>
<th>B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cv (J/mol/K)</td>
<td>1.87</td>
<td>1.82</td>
<td>1.82</td>
<td>1.82</td>
<td>1.82</td>
<td></td>
</tr>
<tr>
<td>S (J/mol/K)</td>
<td>6.98</td>
<td>7.19</td>
<td>7.19</td>
<td>7.19</td>
<td>7.19</td>
<td></td>
</tr>
</tbody>
</table>

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 (-670,71 a.u.) of Eelec at B3LYP shows us that the compound is most stable and the highest value (6689,35 eV) in RHF is less stable.

The correlation effect of electron is observed on figure 5 for the values of (EI, AE) and (Ept).

This compound constitutes an attractive object for future studies of NLO properties, because of its higher values of the electronic parameters.

B3LYP and MPW1PW91 are well defined to produce the best results of our study.

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LITERATURE CITED