

Structure, Electronic and Nonlinear Optical Properties of Furyloxazoles and Thienyloxazoles

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Abstract. Geometry optimization, electronic and nonlinear optical properties of isomers of furyloxazole and thienyloxazole molecules are carried out at the B3LYP/6-311++G(2d,p) level. The conformational analysis of 12 compounds have been studied as a function of torsional angle between rings. Electronic and NLO properties such as dipole moment, energy gap, polarizability and first hyperpolarizability were also calculated.

1. Introduction

Thiophene, furan and oxazole are five membered heterocyclic aromatic molecules. They have been studied extensively in the literature because of their wide applications in various areas of science and industry [1-3]. Also, they are important building blocks for new materials possessing interesting electronic, mechanical and biological properties [2,3]. Discrete oligomers and their polymers such as polythiophenes, and polyfurans are widely studied by experimentally and computationally [4,5]. There have been few reports on mixed these oligomers and other five or six membered heterocycles. Quantum mechanical methods are able to describe the geometric and electronic structure of such kind of compounds in good agreement with experimental data. Theoretical investigations have been reported addressing the torsion potential of 2,2'-bithiophene, and bifuran, [6-7]. A literature review can be found in these references. It becomes interesting to study composite molecules made of thiophene, furan and oxazoles. When two units connected together by a single bond they produce new composite molecules such as furyloxazoles and thienyloxazoles. Each of them have six isomers. It is important to understand their molecular structure and physical quantities to provide guidelines for the development of new materials.

Furyloxazoles and thienyloxazoles are composite molecules having subunits as furan and thiophene monomers connected to oxazole monomer by a single bond, respectively. Each of them have six structural isomers. The subunit molecules can rotate around the single bond linking them together. The aim of present work is to obtain theoretical data of the structure, conformation, dipole moment, highest occupied molecular orbital energy (HOMO) and lowest unoccupied molecular orbital energy (LUMO) differences that is energy gap, dipole polarizability, and first hyperpolarizability of isomers of furyloxazole and thienyloxazole molecules.



2. Computations and Methodology

All the quantum chemical DFT calculations were performed with the Gaussian03 program [8]. The B3LYP hybrid functional of Becke [9,10] was employed here in combination with the 6-311++G(2d,p) basis set [11-12] for all calculations. The equilibrium geometries of 12 isomers of furyloxazole and thienyloxazole molecules have been obtained through geometry optimization. Vibrational frequencies were calculated to confirm the equilibrium geometries corresponding to the energy minima. The conformational analysis of all compounds have been studied as a function of inter-rings C-C dihedral angle varying between 0° and 180° with a step of 15°. Electronic and nonlinear optical (NLO) properties such as dipole moment, HOMO-LUMO energy gap, polarizability, anisotropic polarizability and first hyperpolarizability were also calculated. When a molecular system having a permanent dipole moment μ_0 interact with a uniform external electric field E , molecule have an induced dipole moment μ_i as

$$\mu_i = \mu_0 + \alpha_{ij}E_{ij} + \beta_{ijk}E_{ijk} + \dots \quad i, j, k = x, y, z \quad (1)$$

Where α_{ij} and β_{ijk} are polarizability and first hyperpolarizability compenets, respectively. The averaged polarizabiliy (α), anisotropic polarizability ($\Delta\alpha$) and total first hyperpolarizability (β) were reported as

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

$$\Delta\alpha = \left\{ \frac{1}{2} \left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2 \right] \right\}^{1/2} \quad (3)$$

$$\beta = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \right]^{1/2} \quad (4)$$

where x, y and z components of α and β were obtained from Gaussian output.

3. Results and Discussion

The Figure 1 depicts the B3LYP/6-311++G(2d,p) optimized structures that completely planar. The changes in the electronic energy terms are caused by internal rotation around C-C bond between rings can be revealed by keeping all other geometry parameters fixed. In Figures 2 and 3 the relative torsion energy as a function of torsion angle are presented where the energy of global minimum structure is taken as a zero level.

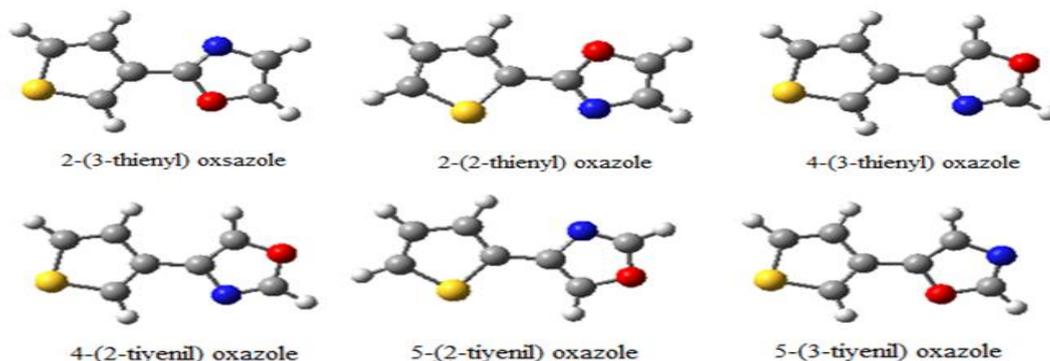


Figure 1. Molecular structures of thienyloxazoles (grey ball: C, white ball:H, blue ball:N, red ball:O, yellow: S. For furyloxazoles yellow:O).

Figures 2 and 3 show that there are two minima on the potential energy surface. We take global minimum at 0° , and local minimum at 180° . The height of rotational barrier at 90° fall within the range between $3.8\text{-}6.4\text{ kcal.mol}^{-1}$ and $3.9\text{-}6.0\text{ kcal.mol}^{-1}$ for thienyloxazoles and furyloxazoles, respectively.

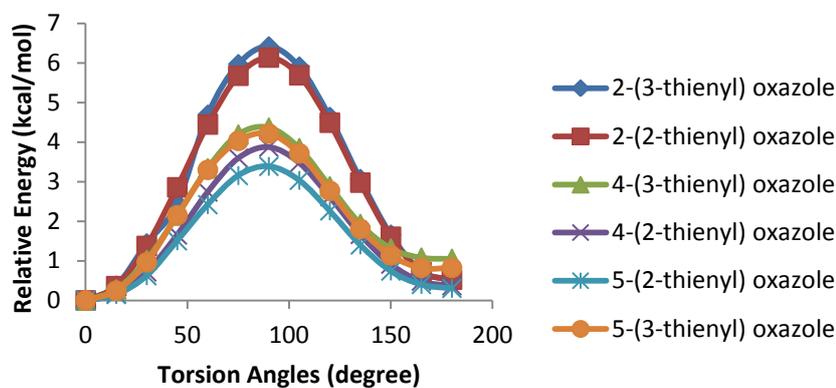


Figure 2. Relative torsion energies for thienyloxazoles.

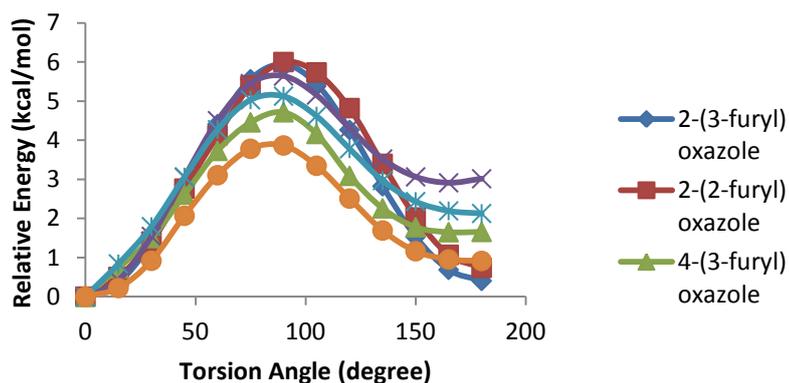


Figure 3. Relative torsion energies for thienyloxazoles.

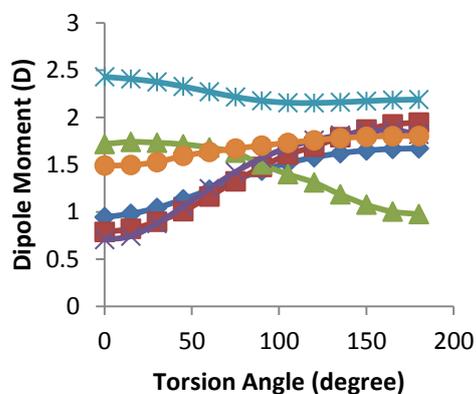


Figure 4. Dipole moments for thienyloxazoles.

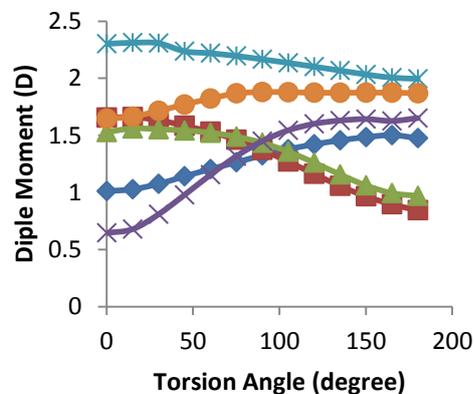


Figure 5. Dipole moments for thienyloxazoles.

Dipole moment is an important descriptor of charge distribution in a molecule. The dipole moments are given in Tables 1 and 2 and in Figures 3 and 4 as a function of torsion angle. Figures show that dipole moment values of studied molecules are heavily depend on torsion angle with exceptions. The B3LYP/6-311++G(2d,p) calculated electric dipole moment, (H-L) energy gap, polarizability, anisotropic polarizability and first hyperpolarizability values are given in Table 1 and 2 for thienyloxazoles and furyloxazoles, respectively.

Table 1. Calculated electric dipole moment, (H-L) energy gap, polarizability, anisotropic polarizability and first hyperpolarizability of thienyloxazoles.

Molecule	Dipole (Debye)	H-L eV	α (au)	$\Delta\alpha$ (au)	β (au)
2-(3-thienyl) oxazole	1.0118	4.88	112.9	57.6	155.3
2-(2-thienyl) oxazole	1.6556	4.50	114.8	65.8	190.6
4-(3-thienyl) oxazole	1.5288	5.27	91.1	39.1	48.5
4-(2-thienyl) oxazole	0.6462	4.83	109.2	51.0	92.7
5-(2-thienyl) oxazole	2.3022	5.25	114.6	54.8	51.5
5-(3-thienyl) oxazole	1.6461	4.98	94.3	42.6	235.4

Table 1. Calculated electric dipole moment, (H-L) energy gap, polarizability, anisotropic polarizability and first hyperpolarizability of furyloxazoles.

Molecule	Dipole (Debye)	H-L eV	α (au)	$\Delta\alpha$ (au)	β (au)
2-(3-furyl) oxazole	0.9459	5.15	94.5	35.0	100.1
2-(2-furyl) oxazole	0.7889	4.67	100.1	40.8	45.1
4-(3-furyl) oxazole	1.7181	5.50	91.6	30.6	117.1
4-(2-furyl) oxazole	0.7071	4.96	95.5	40.0	25.1
5-(2-furyl) oxazole	2.4286	4.66	99.4	37.5	185.4
5-(3-furyl) oxazole	1.4911	5.15	94.1	32.2	169.1

The HOMO-LUMO energy gap is an important parameter determine the usefulness of molecules in technology. The calculated absolute HOMO-LUMO energy values ranges from 4.66 to 5.50 eV. The dipole polarizability values ranges from 91 to 115 au. The calculated hyperpolarizability values ranges from 45 to 235 au. that shows very low nonlinear optical properties.

4. References

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