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Nonlinear Optical Properties (NLO), HOMO-LUMO Energies and Reactivity Descriptors of 2-Thiophene Carboxylic Acid

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Abstract: In this research nonlinear optical properties such as polarizability, polarizability of anisotropy, first static hyperpolarizability of 2-Thiophene carboxylic acid were calculated with by using Becke three parameter functional(B3LYP) hybrid approaches within the density functional theory. 6-31G (d, p), 6-31++G (d, p), 6-311G (d, p) and 6-311++G (d, p) basis sets were chosen for the analyze of basis set effect on nonlinear optical properties. Furthermore, HOMO–LUMO molecular orbital energy difference were calculated at the stationary point on the energy surface. Also, some reactivity descriptors (such as ionization energy, electron affinity, chemical softness, chemical hardness, electronegativity, chemical potential and electrophilicity index) of 2-Thiophene carboxylic acid were investigated. All calculations performed with Gauss View 5.0 and Gaussian 09 packages.

Keywords: DFT, HOMO-LUMO, NLO, Reactivity Descriptors

I. INTRODUCTION

Investigation of the nonlinear optical properties of the materials is so important due to the key functions of frequency shifting, optical modulation, optical switching, optical logic and optical memory for the emerging technologies in areas such as in telecommunications, information storage, optical switching signal processing [1]and THz wave generation [2]. Nonlinear materials with large optical nonlinearities and fast response speeds are fundamental requirements for future photonics devices. Also, nonlinear absorption is important for sensor protection applications like multiphoton absorption induced optical power limiting. Thus, measurements of the magnitude and the transient response of optical nonlinearities, in particular the nonlinear refractive indices, of materials are becoming increasingly important [3].

Thiophenes are part of many organic compounds, which have wide applications in the fields of electronics and optoelectronics, drugs and materials [4]-[8]. The exceptional

pharmacological activity of compounds containing a thiophene ring in the structure is known for its antidepressant, anticonvulsant, anthelmintic, antispasmodic, antihistaminic, anesthetic, antipruritic, antitussive, analgesic effects [9]. Thiophene and its derivatives exhibit various biological properties such as nematocidal [10], insecticidal [11], antibacterial [12], antifungal [13], antiviral [14] and antioxidant activity [15].

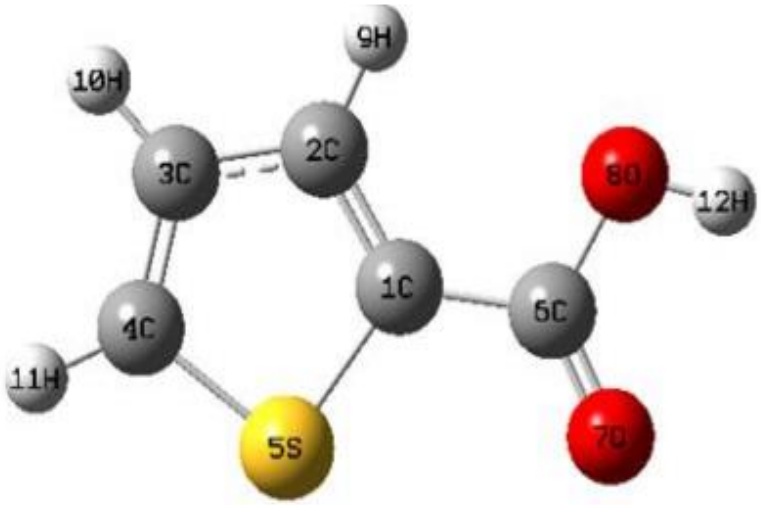

Fig.1. Molecular geometry of 2-Thiophene carboxylic acid

In the present work, we have calculated nonlinear optical properties, by using the density functional theory (DFT) method [16]. Molecular structure of 2-Thiophene carboxylic acid were as shown at Fig. 1. Additionally, frontier molecular orbital energies and some reactivity descriptors were investigated with DFT B3LYP/6-311++G (d, p) level of theory.

II. COMPUTATIONAL DETAILS

Nonlinear optical properties, HOMO-LUMO molecular orbital energies and reactivity descriptors of 2-Thiophene carboxylic acid were calculated with DFT B3LYP method. 6-31G (d, p), 6-31++G (d, p), 6-311G (d, p) and 6-311++G (d, p) were chosen as the basis sets for NLO calculations. Molecular geometry was not restricted and all the calculations were performed by using the Gauss–View molecular visualization program 5.0 and the Gaussian 09 program package on a personal computer [17].

III. RESULTS AND DISCUSSION

A. Nonlinear Optical Properties (NLO)

Polarizability characterizes the ability of an electric field to distort the electronic distribution of a molecule. Higher order polarizabilities (hyperpolarizabilities) which describe the nonlinear response of atoms and molecules are related to a wide range of phenomenon from nonlinear optics to intermolecular forces, such as the stability of chemical bonds as well as the conformation of molecules and molecular aggregates [18].

The dipole moment (μ), the static polarizability (α) and first static hyperpolarizability (βtot) are related directly to the nonlinear optical (NLO) properties. The total static dipole moment, μ is defined as; $\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)1/2$. The calculations of static polarizability (α_{ave}) and first static hyperpolarizability (βtot) from the Gaussian output have been stated in detail previously [19] as follows:

$<\alpha> = 1/3\ (\alpha xx + \alpha yy + \alpha zz\ )$

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

The first static hyperpolarizability (βtot), mean polarizability (<α>) and the ground state dipole moment (μ) of 2-Thiophene carboxylic acid were calculated by DFT B3LYP method and different ten basis sets. Results presented at Table 1.

First static hyperpolarizability of title compound was computed to be 2.19991 x10-30, 1.91438 x10-30, 2.06557 x10-30 and 3.63913 x10-30 esu for 6-31G (d, p), 6-31++G (d, p), 6-311G (d, p) and 6-311++G (d, p) (respectively). It found that, the first static hyperpolarizability of 2-Thiophene carboxylic acid is 5.90, 5.14, 5.54 and 9.76 times larger than that of urea (0.3728x 10-30esu) for 6-31G (d, p), 6-31++G (d, p), 6-311G (d, p) and 6-311++G (d, p), respectively. These results showed that the 2-Thiophene carboxylic acid is candidate molecule for nonlinear optical applications.

Table 1.

The electric dipole moment μ (D), the mean polarizability <α> and the first hyperpolarizability β_{tot} of 2-Thiophene carboxylic acid by DFT B3LYP method and different ten basis sets

Parameter	6-31G(d,p)	6-31G++(d,p)	6-311G(d,p)	6-311++G(d,p)	Parameter	6-31G(d,p)	6-31G++(d,p)	6-311G(d
μ_x	1.71	1.90	1.66	1.41	$ß_{xxx}$	-310.68	-376.02	-322.79
μ_y	2.71	2.62	2.55	1.71	$ß_{xxy}$	-8.43	-30.81	4.36
μ_z	0.07	0.12	0.09	0.00	$ß_{xyy}$	53.65	74.03	68.74
M	3.20	3.24	3.04	2.22	$ß_{yyy}$	35.87	34.65	6.78
α_{xx}	100.80	110.93	104.01	105.54	$ß_{xxz}$	-0,28	0.48	-0.31
α_{xy}	3.10	4.20	3.04	13.57	$ß_{xyz}$	0.76	0.05	0.09
α_{yy}	83.16	93.68	87.49	107.24	$ß_{yyz}$	-1.39	-0.22	0.21
α_{xz}	0.00	0.00	0.00	0.00	$ß_{xzz}$	3.06	80.73	15.44
α_{yz}	0.00	0.00	0.00	0.00	$ß_{yzz}$	-9.14	8.27	3.91
α_{zz}	30.66	48.30	33.66	48.51	$ß_{zzz}$	-1.21	0.05	-1.29
<α> (a.u)	71.54	84.30	87.09	87.10	β_{tot} (a.u)	254.64	221.59	239.09
<α> (esu)	10.60	12.49	12.90	12.90	β_{tot} (esu)	2199.91	1914.38	2065.57

α: 1a.u = $0.1482*10^{-24}$esu
β: 1a.u = $8.6393*10^{-33}$esu

B. HOMO-LUMO Molecular Orbital Energies

The highest occupied molecular orbital (HOMO) energy and lowest unoccupied molecular orbital (LUMO) energy are used to explain several types of reactions and for predicting the most reactive position in conjugated systems and chemical reactivity descriptors [20].

While the HOMO is directly related to the ionization potential, the LUMO is directly related to the electron affinity. The molecules with a larger $\Delta E_{HOMO-LUMO}$ band gap should be less reactive than one having a smaller gap [21]. The frontier molecular orbital distributions and energy levels of the HOMO and LUMO, which computed at B3LYP/6-311++G(d,p) level of studied compound were shown in Fig. 2.

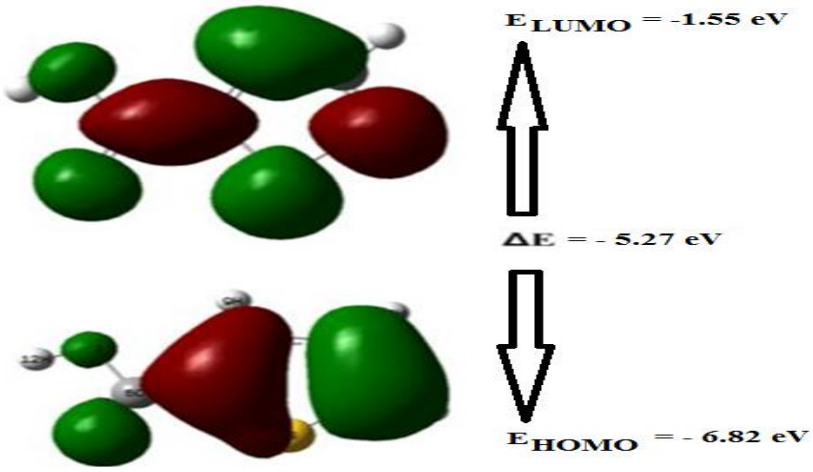

Fig.2. Molecular orbital energy diagram and energy band gap of 2-Thiophene carboxylic acid

Energy band gap of 2-Thiophene carboxylic acid molecule ($\Delta E_{HOMO-LUMO}$) was found to be 5.27 eV at B3LYP/6-311++G(d,p) in gas phase. The ionization energy and electron affinity can be expressed through HOMO and LUMO orbital energies according to the Koopman's theorem [22];

$I = -E_{HOMO}$

$A = -E_{LUMO}$

In the past, the hardness has been associated with the stability of chemical system [23]. The chemical hardness corresponds to the gap between the HOMO and LUMO orbitals. The larger HOMO-LUMO energy gap is the harder molecule.

$\eta = \frac{1}{2}(E_{LUMO} - E_{HOMO})$

The chemical softness is as follows,

$S = \frac{1}{2\eta}$

Electro negativity is a measure of the tendency of an atom to attract a bonding pair of electrons.

$\chi = \frac{1}{2}(I+A)$

Electronic chemical potential μ defined by Parr and Pearson [24] as follow;

$\mu = -\frac{1}{2}(I+A) = \frac{1}{2}(E_{HOMO} + E_{LUMO})$

Table 2. Calculated values for frontier orbital energies, energy band gap (ΔE), ionization energy (I), electron affinity(A), electro negativity(χ), chemical hardnesses (η) and chemical softness (S), chemical potential (μ) and global electrophilicity index (ω) of 2-Thiophene carboxylic acid

Physical properties	B3LYP/6-311++G(d,p)
E_{HOMO} (eV)	-6.82
E_{LUMO} (eV)	-1.55
$\Delta E = E_{HOMO-LUMO}$ (eV)	5.27
I (eV)	6.82
A (eV)	1.55
χ (eV)	4.185
η(eV)	2.635
S (eV^{-1})	0.189
μ (eV)	-4.185
ω (eV)	3.323

The global electrophilicity index ω was introduced by Parr [25] and calculated as follow equation;

$\omega = \mu^2/2\eta$

All the calculated parameters were given in Table 2.

IV. CONCLUSION

In this research, nonlinear optical properties of 2-Thiophene carboxylic acid investigated with DFT B3LYP method and 6-31G (d, p), 6-31++G (d, p), 6-311G (d, p) and 6-311++G (d, p) basis set. Also, HOMO-LUMO molecular orbital energies and some reactivity descriptors were calculated with B3LYP/6-311G(d,p) level of theory. Computations show that first static hyperpolarizability of 2-Thiophene carboxylic acid is about 9.76 times larger than that of urea. According to results 2-Thiophene carboxylic acid is candidate system for nonlinear optical applications.

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