Journal of King Saud University – Science (2017) **29**, 70–83

King Saud University
Journal of King Saud University – Science
www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Investigation on the key features of L-Histidinium 2-nitrobenzoate (LH2NB) for optoelectronic applications: A comparative study

Mohd. Shkir *

Department of Physics, Faculty of Science, King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia

Received 14 October 2015; accepted 10 March 2016
Available online 3 May 2016

KEYWORDS

Organic compounds;
Raman spectroscopy and scattering;
Optical materials;
Nonlinear optical material;
Computational techniques

Abstract The current work is to highlight the fundamental acumen about the molecular structure, photophysical and static first hyperpolarizability (β) of L-Histidinium 2-nitrobenzoate (LH2NB) organic molecule for the first time. Hartree–Fock (HF) and density functional theory (DFT) has been applied using different functional at 6-31G** basis set for the first time. The strong correlation has been observed between experimental and theoretical vibrational spectra. TD-DFT method has been used at different levels of theory to study the UV–Visible spectra. The analysis of HOMO and LUMO was done to explain the charge interaction taking place within the molecule and the energy gap was evaluated. The value of dipole moment is found to be lower in excited state than ground state as calculated from all applied methods. The value of total static first hyperpolarizability was found to be 7.447×10^{-30} esu at B3LYP/6-31G** level of theory, which is about 20 times higher than urea molecule. The current results indicate that the studied molecule may be a decent applicant for opto-electronic applications.

1. Introduction

Since last few decades the research and development on L-Histidine and its complexes has been receiving an immense attention due to their easy synthesis, growth and good nonlinear optical (NLO) properties and hence emerges as one of the most extensively explored amino acid from its family. It can forms a variety of complexes with different organic and inorganic materials such as: gold (III)–L-histidine (Cuadrado et al., 2000), L-Histidinium 2-nitrobenzoate (Moovendaran et al., 2013; Natarajan et al., 2012), l-histidine-4-nitrophenolate 4-nitrophenol (LHPP) Dhanalakshmi et al., 2010, l-histidine acetate (Madhavan et al., 2007), L-Histidinium perchlorate (LHPCL) Aruna et al., 2007, l-Histidine nitrate (Dhas and Natarajan, 2008), L-histidinium trifluoroacetate (Dhas et al., 2008), l-histidine hydrofluoride dihydrate (LHHF) Madhavan et al., 2006, l-histidine hydrochloride monohydrate (Anandan and Jayavel, 2011; Madhavan et al., 2007), and l-histidine

---

* Address: Department of Physics, College of Science, King Khalid University, Saudi Arabia. Tel.: +966 530683673; fax: +966 72418319.
E-mail addresses: shkirphysics@gmail.com, shkirphysics@kku.edu.sa.

Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jksus.2016.03.002
1018-3647

bromide (Ahmed et al., 2008) and shows noticeable Second Harmonic Generation (SHG) efficiency. L-Histidine has another important advantage of being an organic material, which is well known due to its low cost, extraordinary nonlinearity, high optical threshold, synthetic litheness, and easy molecular design. Also its configuration can be modified to get the desired nonlinear optical (NLO) properties for tailor made applications and also shows low dielectric constants which makes it useful in terahertz (THz) generation devices (Boomadevi et al., 2004; Moovendaran et al., 2012; Zyss et al., 1984; Chemla, 2012; Shakir et al., 2010, 2014; Ledoux et al., 1987; Fujiwara et al., 2006; Shakir et al., 2009).

The synthesis of a new L-Histidine compound named L-Histidinium 2-nitrobenzoate (LH2NB) (chemical structure shows in Fig. 1) has been reported (Natarajan et al., 2012), and its crystallization, molecular structure, vibrational, optical, second harmonic generation (SHG) efficiency and thermal properties are described. Moovendaran et al. (2013) has reported the SHG efficiency of titled compound which is about 2 times higher than standard KDP crystal.

As per the current available literature it is clear that only experimental studies have been performed on the titled compound so far. However, it is very important and justified to study its theoretical properties such as geometrical, vibrational, photophysical, nonlinear etc. using HF and density functional theory (DFT) to understand the mechanism responsible for its use in various optoelectronic applications. Hartree–Fock (HF) and DFT show key advantages in calculating the various parameters such as: vibrational frequencies, molecular geometries of different kinds of materials very precisely within short time and at low cost (Johnson et al., 1993; Cinar et al., 2014; Shkir and Abbas, 2014a, 2014b; Arivazhagan and Meenakshi, 2012; Reshak and Khan, 2014; Govindarasu and Kavitha, 2014; Elleuch et al., 2007; Shkir et al., 2014, 2015a, 2015b, 2015c, 2015d). Furthermore, the range separated functionals such as CAM-B3LYP, wb97xd and many more are efficient to calculate the electronic and nonlinear optical (NLO) properties which are much superior to the conventional methods (Johnson et al., 1993; Cinar et al., 2014; Shkir and Abbas, 2014a, 2014b; Arivazhagan and Meenakshi, 2012; Reshak and Khan, 2014; Govindarasu and Kavitha, 2014; Elleuch et al., 2007; Shkir et al., 2014, 2015a, 2015b, 2015c; Abbas et al., 2015).

In the current work, the author's goal is to highlight the key features of LH2NB molecule by HF and DFT (using different functional) studies carried out for the first time. It may be noted here that the reason for applying the different functional is to have a in-depth knowledge about the appropriateness of functional which gives better results for the titled molecule as every functional has different extension of DFT.

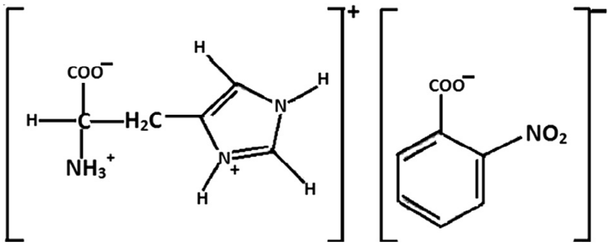

Figure 1 Chemical structure of LH2NB.

2. Computational details

HF (Fischer et al., 1973) and DFT using B3LYP- Becke's three parameter exchange functional B3 combined with Lee–Yang-Parr correlation functional LYP (Becke, 1993; Lee et al., 1988) for obtaining the molecular structures, IR and Raman spectra. Further the TD-DFT study has been performed using B3LYP along with range separated functional such as CAM-B3LYP (Yanai et al., 2004), wb97xd (Chai and Head-Gordon, 2008), PBE0 (Adamo and Barone, 1999), M06 (Zhao and Truhlar, 2008) for calculating opto-electronic properties (Dreuw and Head-Gordon, 2004; Foster and Wong, 2012; Wong et al., 2009; Gibbs et al., 2011). The stable geometry was achieved following the true minimum on the potential energy surface (PES) attained by solving the self-consistent field equation. Infrared (IR) and vibrational (Raman) frequencies were calculated using optimized structural parameters to characterize all stationary points as minima. All the theoretical calculations were made using Gaussian 09W program package (Frisch et al., 2009) with the default convergence principles, without any constraint on the geometry. By applying the different functional the dipole moment, polarizability, anisotropy of polarizability, and static and total first hyperpolarizability values were calculated. Finite Field (FF) method was employed to calculate the value of total first hyperpolarizability (β_{tot}) and its tensor components. FF method was generally applied to know the nonlinear optical properties because this approach can be used in concert with the electronic structure method to work out β values. β_{tot} values calculated by this method is found to be genuine with experimental structure property relationship recently. A static electric field (F) has been applied to a molecule in FF method and the energy (E) is expressed by the following relation:

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

where $E^{(0)}$ is the energy of molecule in the absence of an electric field, μ is components of the dipole moment vector, α is the linear polarizability tensor, β and γ are the first and second hyperpolarizability tensors respectively, while *i,j* and *k* label the *x,y* and *z* components respectively. Values of μ, α, β, and γ can be obtained by differentiating Eq. (1) with respect to *F*.

The value of static hyperpolarizability (β_0) can be calculated from the following equation:

$$\beta_0 = \frac{3}{5}\beta_{tot} \tag{2}$$

Further, the optical absorption spectra were calculated by time dependent DFT (TDDFT) study suing different functional.

GCRD parameters of the titled molecule have been calculated as follows:

A relation for absolute hardness (η) was established Parr and Chattaraj, 1991; Pearson, 1985; Parr and Pearson, 1983 i.e.:

$$\eta = \frac{I - A}{2} \tag{3}$$

where *I* is the vertical ionization potential energy and *A* is vertical electron affinity.