Journal of Molecular Structure 1095 (2015) 100–111

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

# Spectral investigation and theoretical study of zwitterionic and neutral forms of quinolinic acid

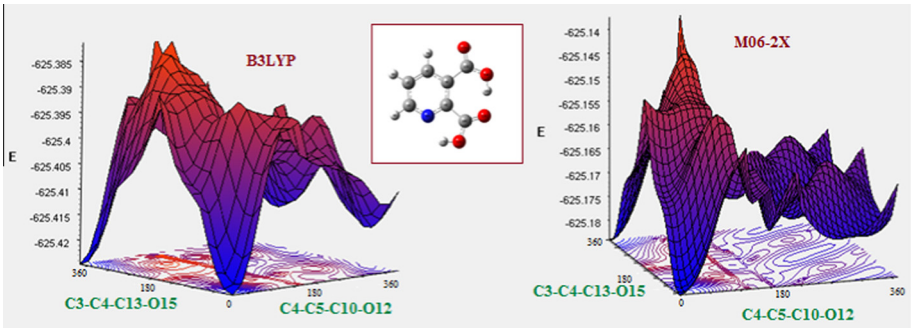
M. Karabacak [a,*], L. Sinha [b], O. Prasad [b], S. Bilgili [c], Alok K. Sachan [b], A.M. Asiri [d,e], A. Atac [c]

[a] Department of Mechatronics Engineering, H.F.T. Technology Faculty, Celal Bayar University, Turgutlu, Manisa, Turkey
[b] Department of Physics, University of Lucknow, Lucknow, India
[c] Department of Physics, Celal Bayar University, Manisa, Turkey
[d] Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia
[e] Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah, Saudi Arabia

## HIGHLIGHTS

- The molecular structures of zwitterionic and neutral forms of quinolinic acid molecule are investigated.
- Spectroscopic features of the compound are examined by UV, FT-IR, FT-Raman, $^{1}H$ and $^{13}C$ NMR techniques and DFT method.
- Thermodynamic features, nonlinear optical properties and frontier molecular orbitals are calculated.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 24 December 2014
Received in revised form 4 April 2015
Accepted 6 April 2015
Available online 18 April 2015

*Keywords:*
Quinolinic acid
FT-IR and FT-Raman
NMR and UV spectra
DFT
Zwitterionic and neutral forms

## ABSTRACT

In this study, molecular structure and vibrational analysis of quinolinic acid (2,3-pyridinedicarboxylic acid), in zwitterionic and neutral forms, were presented using FT-IR, FT-Raman, NMR, UV experimental techniques and quantum chemical calculations. FT-IR and FT-Raman spectra of 2,3-pyridinedicarboxylic acid (2,3-PDCA) in the solid phase were recorded in the region 4000–400 $cm^{-1}$ and 3500–0 $cm^{-1}$, respectively. The geometrical parameters and energies were obtained for zwitter and neutral forms by using density functional theory (DFT) at B3LYP/6-311++G(d,p) level of theory. 3D potential energy scan was performed by varying the selected dihedral angles using M06-2X and B3LYP functionals at 6-31G(d) level of theory and thus the most stable conformer of the title compound was determined. The most stable conformer was further optimized at higher level and vibrational wavenumbers were calculated. Theoretical vibrational assignment of 2,3-PDCA, using percentage potential energy distribution (PED) was done with MOLVIB program. $^{13}C$ and $^{1}H$ NMR spectra were recorded in DMSO. Chemical shifts were calculated at the same level of theory. The UV absorption spectra of the studied compound in ethanol and water were recorded in the range of 200–400 nm. The optimized geometric parameters were compared with experimental data.



## Introduction

Pyridine carboxylic acids are involved in several essential biochemical processes and beneficial compounds for human organism [1]. They are involved in phenylalanine, tryptophan, and alkaloids

* Corresponding author. Tel.: +90 236 314 10 10; fax: +90 236 314 20 20.
*E-mail address:* mehmet.karabacak@cbu.edu.tr (M. Karabacak).

http://dx.doi.org/10.1016/j.molstruc.2015.04.010
0022-2860/

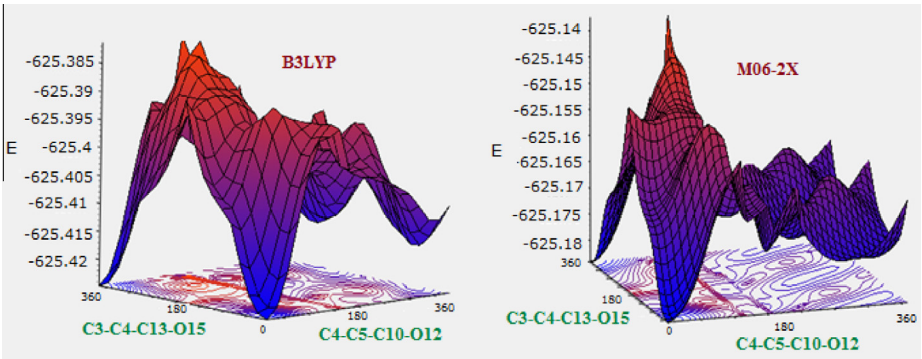



**Fig. 1.** 3D PES of 2,3-PDCA using B3LYP and M06-2X functional at 6-31G(d) basis set. Energy values are in a.u.

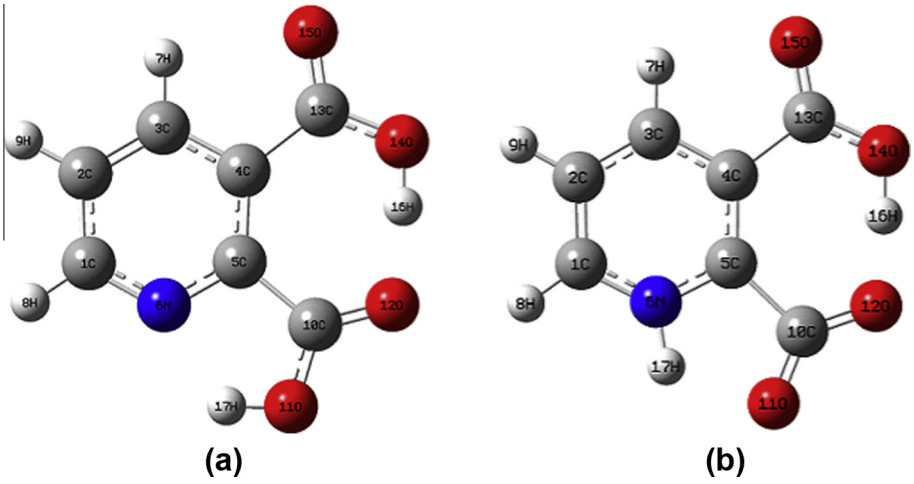



**Fig. 2.** The optimized structures of neutral (a) and zwitterionic (b) forms of 2,3-PDCA molecule.

production, and for the quantitative detection of calcium. They are used as intermediate to produce pharmaceuticals and metal salts for the application of nutritional supplements. The metal complexes of biologically important ligands are sometimes more effective than free ligands [2].

Quinolinic acid or 2,3-pyridinedicarboxylic acid ($C_7H_5NO_4$) is a neuro-active metabolite of the kynurenine pathway. It is usually present in nano-molar concentrations in human brain as well as in cerebrospinal fluid and often associated with several brain diseases such as Alzheimer's disease [3–6], Parkinson's disease [7], motor neuron diseases [8–11], multiple sclerosis [12–14] and Huntington's disease [15–18].

Vibrational modes and theoretical calculations 2,6- and 3,5-pyridinedicarboxylic acid and their calcium and sodium salts were investigated by McCann and Laane [19]. The crystal structure of 2,3-PDCA was determined by X-ray [20] and neutron diffractions [21,22]. In our earlier work, we have fulfilled the theoretical study and vibrational spectra of 3,4-PDCA and 3,5-PDCA [23–25]. However, literature surveys reveals that to the best of our knowledge, neither quantum chemical, nor the vibrational analysis study of 2,3-PDCA has been reported yet. The present work is a continuation of our previous studies on PDCA [23–25]. The importance of 2,3-PDCA in neuron diseases and disorders stimulated us to perform theoretical and experimental (FT-IR, FT-Raman, NMR and UV spectra) spectroscopic analysis of the title molecule along with the calculation of HOMO, LUMO, NLO, thermodynamic properties to get a better insight of the properties of the molecule. Global reactivity descriptors such as hardness, softness, chemical potential, electronegativity, electrophilicity index and local reactivity descriptors like Fukai functions, local softness and local electrophilic indices were computed to predict reactivity and reactive sites on the molecule. UV–Vis spectrum of the title compound was also recorded and the electronic properties, such as Frontier orbitals and band gap energies were measured by TD-DFT approach.

## Experimental

2,3-PDCA in the solid phase was purchased from Merck Company with a stated purity of 97%. The FT-IR spectrum of 2,3-PDCA molecule was recorded between 4000 and 400 $cm^{-1}$ on a Perkin–Elmer FT-IR System Spectrum BX spectrometer, which was calibrated using polystyrene bands. FT-Raman spectrum of the sample was recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 3500–0 $cm^{-1}$ on a Bruker FRA 106/S FT-Raman. The detector is a liquid nitrogen cooled Ge detector. NMR experiments were performed in Varian Infinity Plus spectrometer at 300 K. 2,3-PDCA was dissolved in dimethylsulfoxide (DMSO) and chemical shifts were reported in ppm relative to tetramethylsilane (TMS) for $^1H$ NMR and $^{13}C$ NMR spectra. $^1H$ and $^{13}C$ NMR spectra were obtained at a base frequency of 75 MHz for $^{13}C$ and 300 MHz for $^1H$ nuclei. The UV absorption spectrum of 2,3-PDCA was examined in the range of 200–400 nm using Shimadzu UV-1700 PC, UV–Vis recording Spectrophotometer. The UV pattern is taken from a $10^{-5}$ molar solution of 2,3-PDCA, solved in ethanol and water.