Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 113 (2013) 72–79

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Vibrational spectra of quinoline-4-carbaldehyde: Combined experimental and theoretical studies

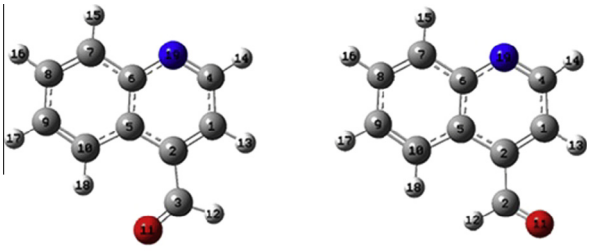
M. Kumru *, V. Küçük, P. Akyürek

Department of Physics, Faculty of Arts and Sciences, Fatih University, Büyükçekmece, 34500 Istanbul, Turkey

HIGHLIGHTS

- The conformational analysis of quinoline-4-carbaldehyde was performed.
- The calculated HF and B3LYP results were compared with experimental FT-IR, FT-FIR, FT-Raman and Dispersive Raman data.
- Frequencies and optimized geometry of *Rot 1* and *Rot 2* conformers of quinoline-4-carbaldehyde were calculated.
- Thermodynamic properties and their correlation with temperature were obtained from the theoretical vibrations.

GRAPHICAL ABSTRACT



Quinoline-4-carbaldehyde

ARTICLE INFO

Article history:
Received 10 May 2012
Received in revised form 11 October 2012
Accepted 24 April 2013
Available online 3 May 2013

Keywords:
Quinoline-4-carbaldehyde
IR spectra
Raman spectra
Normal mode
HF
DFT

ABSTRACT

The FT-IR (4000–50 cm^{-1}), FT-Raman (4000–50 cm^{-1}) and Dispersive-Raman (3500–50 cm^{-1}) spectra of solid sample of quinoline-4-carbaldehyde (Q4C) have been recorded. The molecule structure, vibrational frequencies, IR intensities, Raman intensities and thermodynamic properties of the two possible aldehyde rotamers of Q4C have been obtained with the Hartree–Fock (HF) and density functional B3LYP calculations employing the 6-311++G(d,p) basis set. Q4C has two stable conformers, in one of which the O atom of the aldehyde is oriented to form a H-bond with one of the hydrogens of quinoline, while in the other there is no such a H bond. The conformer with an extra H-bond is more stable and, thus it is the ground state. The computed vibrational frequencies of the lowest energy conformer agree also slightly better than those of the higher energy rotamer with the experimental frequencies after the computed frequencies are scaled. The temperature dependence of the standard heat capacities (C), standard entropies (S) and standard enthalpy (H) changes of Q4C has been discussed.

Introduction

Quinoline (1-azanaphthalene) derivatives, which are composed of benzene fused to a pyridine at two adjacent carbon atoms, have biological and pharmaceutical importance. Quinoline and it derivatives have been extensively studied for their applications in the field of antifilarial [1], biological [2–5], antibacterial [6,7], antimalarial [8–13] and antituberculosis [14] activities. Their magnetic and spectral properties are also of great importance [15]. 4-Quinolinecarboxylate was also shown to form one-dimensional metal–organic coordination polymer [16].

IR and Raman spectra of quinoline were discussed previously [17,18]. In this study, we investigate structure and vibrational spectra of quinoline-4-carbaldehyde (4-CHO-quinoline) abbreviated as Q4C in the following. We firstly report FT-IR (at mid and far regions), FT-Raman and Dispersive-Raman spectra of Q4C that has two stable conformers due to rotation of the aldehyde group. Then, we compare these spectra with our present calculated spectra at HF and B3LYP levels employing with the 6-311++G(d,p) basis

* Corresponding author. Tel.: +90 212 866 34 04; fax: +90 212 866 34 02.
E-mail address: mkumru@fatih.edu.tr (M. Kumru).

1386-1425/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2013.04.088

set for both rotamers. We assign experimental vibrational frequencies to the modes comparing experimental and calculated spectra. We also discuss thermodynamic properties of Q4C.

Experimental details

Q4C with 97% purity was purchased from Alfa Aesar, USA, and used without any further purification. The room temperature mid Fourier Transform IR (FT-IR) spectrum of Q4C (4000–650 cm^{-1}) were recorded by Nicolet 6700 FT-IR spectrometer with attenuated total reflectance (ATR) sampling technique, in which the sample is directly inserted into the spectrometer. However, the room temperature far FT-IR (FT-FIR) spectrum of Q4C (650–50 cm^{-1}) was recorded with PE pellet by using Nicolet 6700 FT-IR spectrometer.

The best quality for the FT-FIR spectra was obtained when the sample/PE ratio of the PE pellets is around 1/10. The PE and the sample were mixed ground in a mortar. The metallic anvil die was heated to 240 °C on a heater until its red light turns off. The temperature was expected to be approximately 130–150 °C (the melting temperature of PE is 120–130 °C). The mixture of PE and the sample are quickly added in the die, which is assembled and put under 5-tons pressure for 2 min. Then, the die is disassembled and the resulting PE pellet was placed into the spectrometer to record the FT-FIR spectrum [19].

The FT-Raman spectrum of Q4C was recorded with Nicolet spectrometer 6700 in the range of 4000–50 cm^{-1} at the room temperature with the 1024 nm wavelength Nd:YAG laser. The Dispersive-Raman spectrum of Q4C was recorded with Dispersive Raman Microscope (DXR) in the range 3500–50 cm^{-1} at the room temperature with the laser of 780 nm wavelength. The recorded FT-IR, FT-FIR, FT-Raman and Dispersive-Raman spectrum of Q4C are shown in Figs. 1–4, respectively.

Quantum chemical calculations

The optimized geometry parameters, vibrational frequencies and thermodynamic properties of Q4C have been obtained at HF and B3LYP levels with the 6-311++G(d,p) basis set. The 6-311G++(d,p) basis set adds polarization functions in the form of five d-type functions for each atom other than H and a set of three p-type polarization functions to the hydrogen atom. It also adds one s-type diffuse function on each atom and one p-type diffuse function on each atom other than hydrogen. These computational levels and the basis set used were already shown useful for

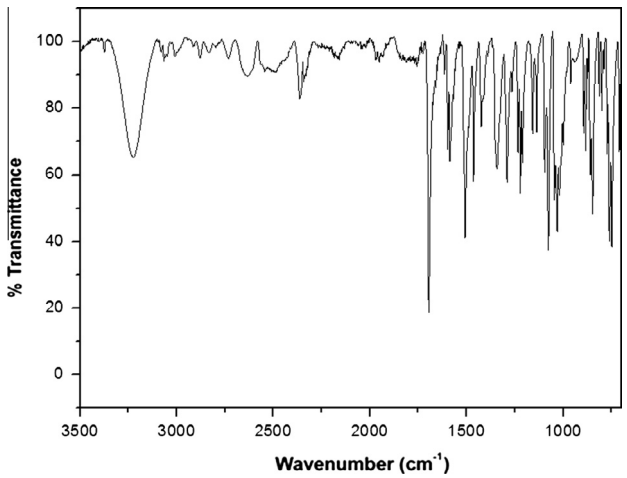


Fig. 1. FT-IR spectrum of Q4C.

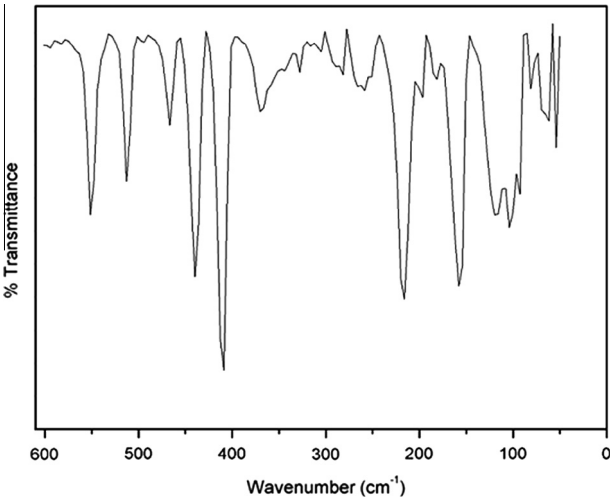


Fig. 2. FT-FIR spectrum of Q4C.

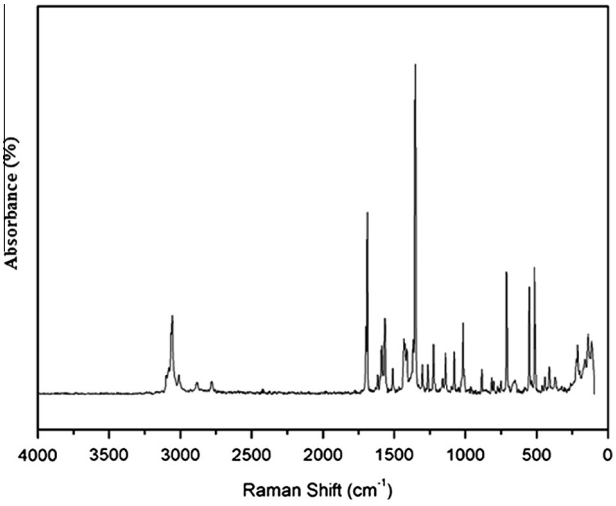


Fig. 3. FT-Raman spectrum of Q4C.

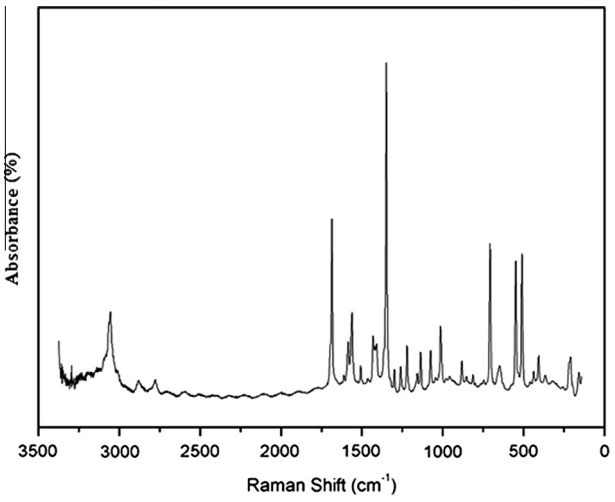


Fig. 4. Dispersive Raman spectrum of Q4C.