Spectrochimica Acta Part A 78 (2011) 319–326

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Vibrational spectra and DFT study of anticancer active molecule 2-(4-Bromophenyl)-1H-benzimidazole by normal coordinate analysis

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ARTICLE INFO

Article history:
Received 27 July 2010
Received in revised form
21 September 2010
Accepted 1 October 2010

Keywords:
Vibrational spectra
DFT calculation
PES scan
Normal coordinate analysis
NBO analysis
ICT

ABSTRACT

FT-IR and FT-Raman spectra of the 2-(4-Bromophenyl)-1H-benzimidzole were recorded and analyzed in the solid phase. The optimized molecular geometry, the vibrational wavenumbers, the infrared intensities and the Raman scattering activities were calculated by using Hartree–Fock and density functional method (B3LYP) with 6-31G(d,p) basis set. The potential surface scan study was carried out for the conformation of theoretical structure. Detailed interpretation of the vibrational spectra had been carried out with the aid of the normal coordinate analysis. Chemical interpretation of hyperconjugative interaction was done by natural bond orbital analysis.

1. Introduction

Benzimidazoles show different biological activities such as anticancer, antimicrobial, and antihelmintic activities [1]. Benzimidazole derivatives are unique and broad-spectrum class of antirhino/enteroviral agents. They exhibit significant activity against several viruses including HIV, herpes (HSV-1), RNA influenza and human cytomegalovirus (HCVM) [2]. The synthesis of benzimidazoles has received much attention owing to the varied biological activities exhibited by numerous derivatives of these compounds [2,3].

2- substituted benzimidazoles have varied pharmacological activities such as antitumor, antivermious, antiviral, hypertensive, spasmolytic, etc. [3,4]. Spectroscopic studies of certain benzimidazole derivatives are already reported [5,6]. Recently density functional theory (DFT) has emerged as a powerful tool for analyzing vibrational spectra of fairly large molecules. The application of DFT to chemical systems has received much attention because of faster convergence in time than traditional quantum mechanical correlation methods [5–8]. The present work reports a detailed spectroscopic study on 2-(4-Bromophenyl)-1H-benzimidazole (BPHB) using IR and Raman spectra followed by normal coordinate analysis (NCA). The natural bond orbital (NBO) analysis is carried out to interpret hyperconjugative interaction and intramolecular charge transfer (ICT). The calculated value of HOMO–LUMO energy gap is used to interpret the biological activity of the molecule.

2. Experimental

4-Bromobenzaladehyde (3.16 g, 20 mmol) was added to a solution of 1,2-phenylenediamine (2.16, 20 mmol) in 50 ml of acetonitrile and refluxed for 2.5 h to synthesis BPHB by reported method [9,10]. Infrared spectrum was taken with a Perkin Elmer RXI spectrometer in the region 4000–400 cm^{-1} with samples in KBr pellet. The NIR-FT-Raman spectrum of a solid BPHB sample was recorded on a Bruker RFS 100/S FT – Raman spectrophotometer in the range 3600–10 cm^{-1}.

3. Computational details

GAUSSIAN 03 [11] software package was used for theoretical calculation. The quantum chemical calculations were performed applying DFT method, with Beeke-3-Lee-Yang-Parr (B3LYP) supplemented with the standard 6-31G(d,p) basis set. The optimized geometry corresponding to the minimum on the potential energy surface has been obtained by solving self-consistent field equation

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doi:10.1016/j.saa.2010.10.013

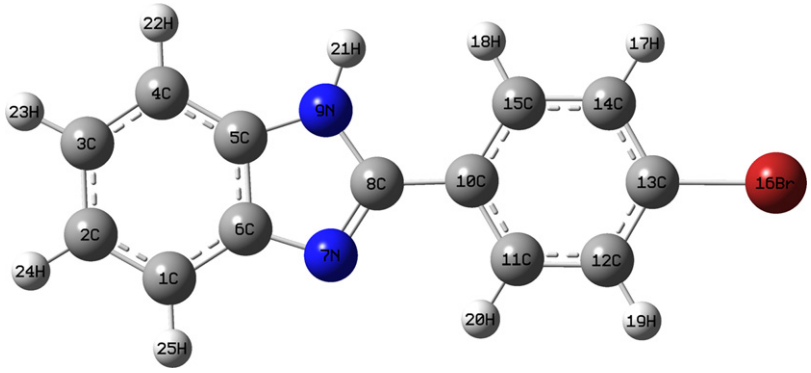

Fig. 1. Optimized structure of BPHB monomer.

iteratively. The harmonic vibrational wavenumbers have been analytically calculated by taking the second order derivative of energy using the same level of theory. The Raman activities (S_i) calculated by Gaussian 03 program has been converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering:

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i[1 - \exp((-hc\nu_i)/(kT))]} \quad (1)$$

where ν_0 is the exciting wavenumber; ν_i the vibrational wavenumber of the normal mode; h, c and k are the universal constants, and f is the suitably chosen common normalization factor for all the peak intensities. Scaling of the force field was performed according to scaled quantum mechanical (SQM) procedure [12,13] using selective scaling in the natural internal coordinate representation [14,15]. Normal coordinate analysis was performed to obtain full description of the molecular motion pertaining to the normal modes using MOLVIB program version 7.0 written by Sundius [16,17]. Geometrical parameters obtained from DFT calculation was then used to perform NBO analysis by the NBO 3.1 program [18] implemented in Gaussian 03 at DFT/B3LYP level in order to understand various second order interaction between the filled orbital of another subsystem, which is a measure of the delocalization or hyperconjugation. The hyperconjugation interaction energy was deduced from the second-order perturbation approach:

$$E^{(2)} = -n_\sigma \frac{\langle\sigma|F|\sigma\rangle^2}{\varepsilon_{\sigma*} - \varepsilon_\sigma} = -n_\sigma \frac{F_{ij}^2}{\Delta E} \quad (2)$$

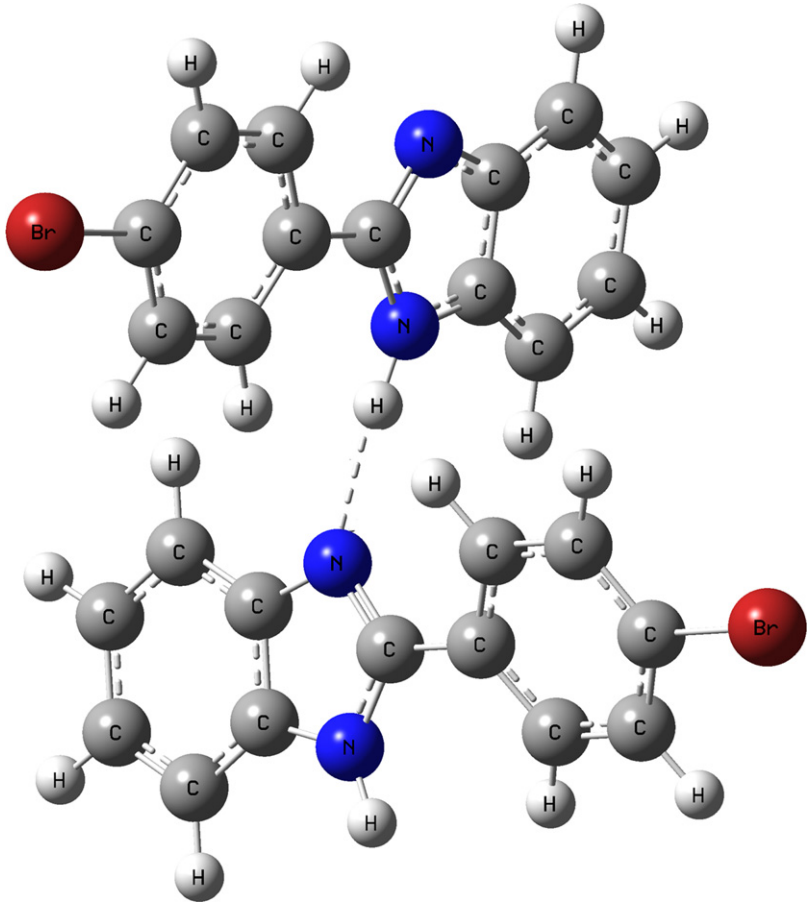

Fig. 2. Optimized structure of BPHB dimer.