



Synthesis, vibrational spectral and nonlinear optical studies of N-(4-hydroxy-phenyl)-2-hydroxybenzaldehyde-imine: A combined experimental and theoretical investigation

Yufeng Wang^a, Zongxue Yu^{a,c}, Yuxi Sun^{a,b,*}, Yishi Wang^a, Lude Lu^a

^a Key Laboratory for Soft Chemistry and Functional Materials of Education Ministry, Nanjing University of Science & Technology, Nanjing 210094, PR China

^b Key Laboratory of Life-Organic Analysis, School of Chemistry & Chemical Engineering, Qufu Normal University, Qufu, 273165, PR China

^c School of Chemistry & Chemical Engineering, Southwest Petroleum University, Chengdu, 610500, PR China

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ABSTRACT

The study of imine-bridged organics has been the one hot spot of photo-responsive material sciences in recent years. Herein we make a study of the synthesis, characteristics and potential application of N-(4-hydroxy-phenyl)-2-hydroxy-benzaldehyde-imine (HPHBI), C₁₃H₁₁NO₂. The studied compound was synthesized in one step by the condensation reaction of salicylaldehyde and 4-aminophenol in methanol solution, and characterized by single crystal X-ray diffraction, FT-IR and FT-Raman techniques with theoretical calculations at B3LYP/6-31G(d) level. The molecule adopts *trans* configuration about central C=N bond with intramolecular hydrogen bonding, and the adjacent molecules form wave-shaped structure linked by strong intermolecular hydrogen bonding mechanism along *b* axis. The vibrational spectra have been precisely assigned with the aid of theoretical frequencies. Furthermore, the thermodynamic properties have been obtained by the theoretical vibrational analysis for HPHBI. The total linear polarizability and first-order hyperpolarizabilities calculated on the studied compound respectively present 25.378 Å³ and 1.655 × 10⁻²⁹ cm⁵/esu, which indicates the compound has relatively good nonlinear optical property.

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1. Introduction

Recently, the heterojunction organics have attracted increasing attention due to their potential applications in optical communications, optoelectronic materials, biofunctional compounds, especially, excellent nonlinear optical (NLO) responses [1–7]. As we know that the heterojunction units are the core structures of a number of natural products as amine acids, DNA, bioelectric or photovoltaic materials. Schiff bases have been proved to be a class of functionally active compounds. For example, Hadjoudis et al. have found that some Schiff base compounds exhibit thermochromism or photochromism properties [8]. Ünver et al. have reported the structural and NLO properties for some imine-bridged aromatic compounds [1,7,9]. Our group has been engaged in the study of the synthesis and NLO properties of a series of imine-bridged antipyrine derivatives for several years [3–6,10–13].

Generally, organic compounds with aromatic moieties can easily transport electrons or charges via/among their conjugated segments to perform photoelectric or NLO effects. Currently, the

organics with electron-donating and electron-withdrawing groups have been regarded as an interesting kind of NLO compounds better than inorganic materials [1,14], wherein, the imine-bridged benzene derivatives have shown high optical nonlinearities. As a result, these compounds are of considerable current research interest in the photo-responsive materials in recent years.

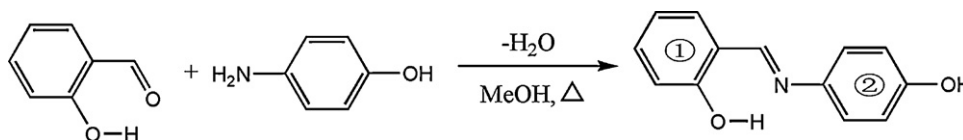
As a heterojunction model compound, N-(4-hydroxy-phenyl)-2-hydroxy-benzaldehyde-imine (HPHBI) (Scheme 1) was synthesized and characterized by X-ray crystal diffraction, FT-IR, FT-Raman techniques, furthermore, the thermodynamic and NLO properties of the studied compound were obtained by theoretical calculations at B3LYP/6-31G(d) level in this work.

2. Experimental

2.1. Synthesis of the title compound

Most of the chemicals (reagent grade) in this work were purchased from Alfa or Ronghua chemical Corp. and used without further purification. The title compound was synthesized in one step according to the classical condensation of aldehyde and ammonia, and the reaction path is shown in Scheme 1. Salicylaldehyde and 4-aminophenol with an equal mole ratio were dissolved in

* Corresponding author. Tel.: +86 25 84303229; fax: +86 25 84315054.
E-mail address: yuxisun@163.com (Y. Sun).



Scheme 1. Synthetic route for HPHBI.

methanol solution. The reaction mixture was stirred for about an hour under reflux to give an orange clear solution. After allowing the solution to stand in air for 11 d, orange block-shaped crystals had formed at the bottom of the vessel on slow evaporation of the solvent (yield 84.7%).

2.2. FI-IR and FT-Raman measurements

The FT-IR spectra of solid compound was recorded in the range of 4000–400 cm^{-1} in evacuation mode with a scanning speed of 30 $\text{cm}^{-1} \text{min}^{-1}$ and a spectral width of 2.0 cm^{-1} on a Bruker IFS 66V FI-IR spectrometer using KBr pellet technique.

The FT-Raman spectrum of HPHBI was measured on RENISHAM inVia Raman microscope equipped with a counter current detector and a diode laser (785 nm line of Nd-YAG laser as excitation wavelength) in the region 4000–100 cm^{-1} with a spectral resolution of 1.0 cm^{-1} in the backscattering configuration.

2.3. X-ray determination

A suitable single crystal was attached to a glass fiber. Data were collected at 295(2) K on a Bruker AXS SMART APEX area-detector diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) with SMART [15] as a driving software; data integration was performed by SAINT-Plus software [16] with multiscan absorption correction applied using SADABS [17]. The crystal structure was solved by a direct method based on difference Fourier and refined by least squares on F^2 with anisotropic displacement parameters for non-H atoms. All of H atoms attached to C/O were placed in calculated positions. All the calculations to solve the structure, to refine the proposed model, and to obtain the derived results were carried out with the computer programs of SHELXS-97 [18], SHELX-L97 [18] and SHELXTL [19]. Full use of CCDC package was also made for searching in the CSD database.

3. Theoretical

In this work, the quantum chemical study was used to make definite assignments for the fundamental normal modes, and to clarify the experimental FT-IR and FT-Raman spectral bands, and to give additional thermodynamic functions and nonlinear optical properties for the title compound.

For meeting the requirements of accuracy and economy, the theoretical method and basis set should be considered firstly. The density functional theory (DFT) has been proved to be extremely useful in treating electron relativities, and the basis set of 6-31G(d) has been used as a very effective and economical level for many organic molecules [20]. Based on the points, the density functional Becke3–Lee–Yang–Parr (DFT/B3LYP) with standard 6-31G(d) basis set was adopted to compute the properties of the studied compound in this work. All the calculations were performed using Gaussian 03W program package [21] with the default convergence criteria.

For the investigated molecule, the initial geometrical configuration was generated from its X-ray diffraction (XRD) crystallographic data, and the optimized geometry corresponding to the minimum on the potential energy surface was obtained by solving self-consistent field equation iteratively without any constraints. The

harmonic vibrational frequencies were analytically calculated by taking the second order derivative of energy using the same level of theory. Normal coordinate analysis was performed to obtain full description of the molecular motion pertaining to the normal modes using the GaussView program [22]. Simultaneously, the statistical thermodynamic functions were theoretically predicted by the harmonic frequencies of the optimized structures for the title compound.

The Raman scattering activities (S_i) calculated by Gaussian 03W program were suitably converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering stated in previous Refs. [23,24]:

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

where ν_0 is the exciting frequency (in cm^{-1} units), ν_i is the vibrational wavenumber of the i th normal mode, h , c and k are universal constants, and f is the suitably chosen common scaling factor for all the peak intensities.

The nonlinear optical (NLO) properties can be obtained by the previously stated methods [13,25–35]. In this work, using the x , y , z components, the total static dipole moment (μ_0), linear polarizability (α_0) and first-order hyperpolarizability (β_0) are calculated by the following equations defined in previous Refs. [13,31–34]:

$$\mu_0 = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \quad (2)$$

$$\alpha_0 = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \quad (3)$$

$$\beta_0 = \sqrt{(\beta_{xxx} + \beta_{xyy} + \beta_{zzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xzx} + \beta_{yyz})^2} \quad (4)$$

4. Results and discussion

4.1. Geometric structure

The molecular structure of HPHBI with the atom-numbering scheme is shown in Fig. 1. X-ray single crystal structure determination indicates the cell structure of the title compound contains eight independent structural units belonging to monoclinic system with space group of $C2/c$. So, the molecule packing structure belongs to the C-face central lattice with one diadaxis along b axis and one glide reflection plane along c axis (Fig. 2(a)), which is different from the reported crystal parameters [36]. The crystallographic data and

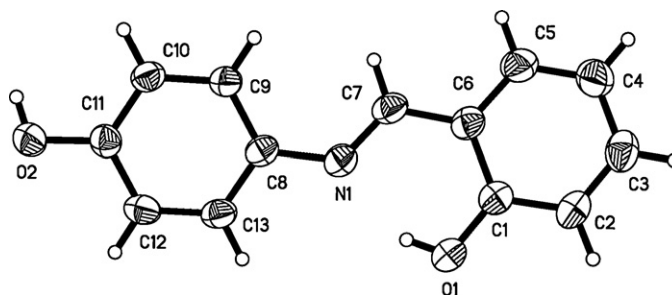


Fig. 1. The molecular structure of HPHBI. The displacement ellipsoids are plotted at the 30% probability level.

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