

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



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

Structural, proton-transfer, thermodynamic and nonlinear optical studies of (*E*)-2-((2-hydroxyphenyl)iminiomethyl)phenolate

Yuxi Sun^{a,b,c,*}, Yufeng Wang^c, Zengwei Liu^b, Changliang Huang^b, Cheng Yu^b

^a Research Center of New Energy & Materials, Mianyang Normal University, Mianyang 621000, PR China

^b School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, PR China

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

HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- The title compound (HPIMP) was synthesized in one step by an amineformaldehyde reaction.
- ► The HPIMP molecule adopt *trans* configuration about C=N bond with intramolecular hydrogen bonding.
- ► A proton-transfer characteristic of HPIMP is proved by experimental results of X-ray and FT-IR.
- The vibrational spectra have been precisely ascribed to molecular structure.
- The thermodynamic properties have been obtained by the theoretical vibrational analysis.
- ► The theoretical first-order hyperpolarizabilities is 19.9 times magnitude of urea.

ARTICLE INFO

Article history: Received 23 February 2012 Received in revised form 18 April 2012 Accepted 27 April 2012 Available online 7 May 2012

Keywords: 2-((2-Hydroxyphenyl)iminiomethyl) phenolate X-ray Vibrational spectra Proton transfer Nonlinear optical



ABSTRACT

Recently, the study of imine-bridged organics is interested in proton-transfer and photo-responsive material fields. Herein, we make a investigation on the structural, thermodynamic and nonlinear optical properties of (*E*)-2-((2-hydroxyphenyl)iminiomethyl)phenolate (HPIMP). The structural varieties of the studied compound are characterized by the X-ray single crystal diffraction and vibrational spectral techniques, as well as the vibrational spectral bands are precisely ascribed to the studied structure with the aid of DFT theoretical calculations. The experimental results of the FT-IR and X-ray measurements supply good proofs to reveal the proton-transfer procedures of HPIMP, and exhibit that the studied compound is a good proton-transfer model. In addition, the thermodynamic properties are obtained from the theoretical vibrations of the optimized HPIMP. The linear polarizability (α_0) and first-order hyperpolarizabilities (β_0) respectively present the values of 26.28 Å³ and 7.41 × 10⁻³⁰ cm⁵/esu predicated theoretically by the DFT-B3IYP method at 6-31G(d) level, which indicates that the studied compound is a promising nonlinear optical material candidate.

© 2012 Elsevier B.V. All rights reserved.

Introduction

Recently, the imine-bridged organics attract extensive attention because of their potential applications in the fields of optical communications, optoelectronic materials, optical switching and

^{*} Corresponding author at: Research Center of New Energy & Materials, Mianyang Normal University, Mianyang 621000, PR China. Tel.: +86 816 2200064; fax: +86 816 2200819.

E-mail address: yuxisun@163.com (Y. Sun).

^{1386-1425/\$ -} see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.saa.2012.04.094

biofunctional compounds [1–7]. As we know that the heterojunction units are the core structures of a number of natural products as amine acids, DNA, and bioelectric or photovoltaic materials. Schiff bases used usually as models have been proved to be a class of multifunctional 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 imine-bridged antipyrine derivatives and finds most of them present good NLO properties in recent years [3–6]. Bondar et al. have reported the suppression of the back proton-transfer from Aps85 to the retinal Schiff base in bacteriorhodipsin [10]. Filarowski et al. have reported the intramolecular hydrogen bond and proton transfer reaction in *N*-methyl-2-hydroxybenzylidene amine [11].

The imine-bridged organics often present tautomerism in orthohydroxylated Schiff bases as a result of intramolecular proton transfer between oxygen and nitrogen atoms [12]. Simultaneously, these molecules can lead to charge transfer by forming pull-push structural system due to π -electron conjugated moieties. Currently, the π -bond structure with electron donor and acceptor groups can increase the asymmetric electronic distribution to perform an increased optical nonlinearity [1,13]. Thereby, the iminebridged aromatic derivatives are very promising proton-transfer model compounds and photo-responsive materials. Based on these considerations, we have previously reported the synthesis, crystal structure, vibrational spectra and NLO properties of N-(4-hydroxy-phenyl)-2-hydroxybenzaldehyde-imine [14]. As an further extension of our work, (E)-2-((2-hydroxyphenyl)iminiomethyl)phenolate (HPIMP) (Scheme 1) was synthesized and characterized in details by a combined experimental and theoretical investigation. And the structural, spectral, thermodynamic and nonlinear optical characteristics of the studied compound are gained. Especially, a significant example for proton-transfer research is present by the results measured by X-ray and spectral techniques in this work.

Experimental

Chemical synthesis

All chemicals (reagent grade) were obtained from a commercial source and used without further purification. The title compound was synthesized according to the classical condensation of aldehyde and ammonia [15], and its reaction path is shown in Scheme 1 as well as the preparation technique was explained in previous studies cited above. In the end, the brown prism-shaped crystals were gained at the bottom of the vessel with slow evaporation of the solvent (yield 85.3%).

Physical measurements

FT-IR absorption spectrum was recorded in the range of 4000–400 cm⁻¹ in an evacuation mode with a scanning speed of

30 cm⁻¹ min⁻¹ and a spectral width of 2.0 cm⁻¹ on a Bruker IFS 66 V FI-IR spectrometer using KBr pellet technique.

The FT-Raman spectrum 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 of 4000–100 cm⁻¹ with a spectral resolution of 1.0 cm^{-1} in the backscattering configuration.

The A suitable single crystal was attached to a glass fiber. Data were collected at 295(2) K on a Bruker AXS SMART APEX areadetector diffractometer (MoKa radiation, $\lambda = 0.71073$ Å) with SMART [16] as a driving software; data integration was performed by SAINTPlus software [17] with multiscan absorption correction applied using SADABS [18]. 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 [19], SHELX-L97 [19] and SHELXTL [20]. Full use of CCDC package was also made for searching in the CSD database.

Theoretical

In this work, 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[21]. Based on the points, the density functional Becke3–Lee–Yang–Parr (DFT/B3LYP) method with standard 6-31G(d) basis set was adopted to compute the properties of the studied compound in the present work. All the calculations were performed using Gaussian 03W program package [22] with the default convergence criteria.

As the first step of our calculation, 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 gain full description of the molecular motion pertaining to the normal modes using the GaussView program [23]. Simultaneously, the statistical thermodynamic functions were theoretically predicted by the harmonic frequencies of the optimized structure for the studied 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. [24,25]:

$$I_{i} = \frac{f(v_{0} - v_{i})^{4}S_{i}}{v_{i} \left[1 - \exp\left(\frac{-hcv_{i}}{kT}\right)\right]}$$
(1)



Scheme 1. Synthetic route of HPIMP.

where v_0 is the exciting frequency (in cm⁻¹ units), v_i is the vibrational wavenumber of the *i*th normal mode, *h*, *c* and *k* are universal constants, and *f* is a suitably chosen common scaling factor for all the peak intensities.

The nonlinear optical (NLO) properties can be obtained by the previously stated methods [26–37]. 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. [26,33–36]:

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

$$\alpha_0 = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \tag{3}$$

$$\beta_{0} = \sqrt{\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^{2} + \left(\beta_{yyy} + \beta_{xxy} + \beta_{yzz}\right)^{2} + \left(\beta_{zzz} + \beta_{xxz} + \beta_{yyz}\right)^{2}} \tag{4}$$

Results and discussion

Molecule structure

The X-ray diffraction result proves that the molecular structure and its packing mode of the studied compound are very close to the previous report [38]. In the present case, the salicylaldimine also takes tautomeric keto form, and the strong intra- and intermolecular N—H···O and O—H···O interactions (Table 1) have effect on the same conformations of the studied molecules and their packing structure as the values reported previously [38]. The displacement ellipsoid plots with atomic renumbering are shown in Fig. 1 in order to state better in this work.

An asymmetric unit of the studied compound is made up of two crystallographically independent molecules, but the two molecular structures are nearly close to each other as shown in Table 2. So, one molecular structure in an asymmetric unit was selected as the initial geometry for theoretical calculations in this work, and the atomic numbering of the theoretical molecule is the same as the first molecule of an asymmetric unit. In order to compare with experimental data better, the optimized parameters gained at B3LYP/6-31G level are listed in Table 2.

As seen from Table 2, it can be observed that the experimental and theoretical geometric parameters are not agree with each other completely owing to the two facts, viz., the first one is that a isolated molecule considered in theoretical calculation in gas phase is contrary to the packing molecules with intermolecular interactions recorded in condensed phase in experimental measurement [39], the second one is that a theory derived from reality is generally imperfect with a case. In the studied case, the largest deviations of bond lengths and bond angles between the optimized values and experimental ones are of 0.06 Å and 2.2°, respectively.

Despite the optimized parameters are slightly different from the crystallographical data for the studied compound, the optimized structure depend upon the method and the basis set used in the

Hydrogen bonding parameters for HPIMP^a.

Table 1

Hydrogen bonding	D—H(Å)	H···A(Å)	D···A(Å)	$D - H \cdot \cdot \cdot A(^{\circ})$
$N1-H1N\cdots01$ $N2-H2N\cdots03$ $N2-H2N\cdots04$ $02-H20\cdots03^{i}$	0.86 (4) 0.86 (3) 0.86 (3) 0.820	1.84 (4) 1.88 (3) 2.33 (3) 1.770	2.603 (4) 2.601 (5) 2.656 (4) 2.585 (4)	148.0 (5) 141.0 (5) 103.0 (5) 170.0
04—H40…01 ⁱⁱ	0.820	1.770	2.580 (4)	168.0

^a Symmetry codes: (i) -x, 1 - y, 1 - z; (ii) 1 - x, 1 - y, 1 - z.



Fig. 1. The displacement ellipsoid plots with atomic numbering for HPIMP.

Table 2	
Selected bond lengths (Å) and	bond angles (°) for HPIMP.

Experimental				Theoretical
Bond length (Å)				
N1-C7	1.296 (4)	N2-C20	1.299 (5)	1.335
N1-C8	1.430 (4)	N2-C21	1.428 (4)	1.403
01–C1	1.304 (4)	03–C14	1.317 (4)	1.260
O2-C9	1.355 (4)	04–C22	1.355 (4)	1.365
C1-C2	1.414 (5)	C14–C15	1.405 (5)	1.448
C1-C6	1.420 (5)	C14–C19	1.409 (5)	1.473
C2-C3	1.375 (5)	C15-C16	1.369 (5)	1.368
C3-C4	1.381 (5)	C16–C17	1.381 (5)	1.431
C4—C5	1.357 (5)	C17–C18	1.352 (5)	1.367
C5–C6	1.404 (4)	C18–C19	1.408 (5)	1.431
C6–C7	1.417 (5)	C19–C20	1.418(5)	1.394
C8—C9	1.389 (5)	C21-C22	1.384(5)	1.412
C8-C13	1.362 (5)	C21-C26	1.383 (5)	1.400
C9–C10	1.379 (5)	C22–C23	1.384(5)	1.394
C10-C11	1.360 (5)	C23–C24	1.380(5)	1.396
C11-C12	1.389 (5)	C24–C25	1.373 (5)	1.395
C12–C13	1.387 (5)	C25-C26	1.385(5)	1.395
Bond Angles (°)				
C7-N1-C8	127.4 (3)	C20-N2-C21	126.9 (3)	127.3
01-C1-C2	122.1 (4)	03–C14–C15	120.9 (4)	122.1
01-C1-C6	121.5 (3)	03–C14–C19	122.1 (3)	122.1
C2-C1-C6	116.3 (4)	C15-C14-C19	117.0(4)	115.8
C3-C2-C1	121.0 (4)	C16-C15-C14	120.8 (4)	121.5
C2-C3-C4	121.7 (4)	C15-C16-C17	121.5 (4)	122.0
C5-C4-C3	119.1 (4)	C18–C17–C16	119.7 (4)	119.3
C4-C5-C6	121.1 (4)	C17-C18-C19	120.3 (4)	121.1
C5-C6-C7	118.4 (3)	C18-C19-C14	120.6 (4)	119.7
C5-C6-C1	120.7 (3)	C18-C19-C20	118.1 (3)	120.3
C7-C6-C1	120.9 (3)	C14-C19-C20	121.3 (3)	120.1
N1-C7-C6	123.5 (4)	N2-C20-C19	122.6(4)	123.3
С13—С8—С9	120.6 (3)	C26-C21-C22	120.2 (4)	118.8
C13-C8-N1	122.8 (3)	C26-C21-N2	123.3 (3)	124.1
C9-C8-N1	116.6 (3)	C22-C21-N2	116.5 (3)	117.1
02-C9-C10	123.4 (3)	04–C22–C23	122.9(3)	123.6
02-C9-C8	117.3 (3)	04-C22-C21	117.9(3)	116.2
С10-С9-С8	119.2 (3)	C23-C22-C21	119.3 (4)	120.2
С11-С10-С9	120.5 (4)	C24–C23–C22	120.6 (4)	120.3
C10-C11-C12	120.5 (4)	C25-C24-C23	119.8 (4)	119.8
C13-C12-C11	119.2 (4)	C24-C25-C26	120.2 (4)	120.1
C8-C13-C12	120.1 (4)	C21-C26-C25	119.8 (4)	120.7
Torsion Angles (°)				
C5-C6-C7-N1	-178.7	C18-C19-C20-N2	178.2 (4)	-179.7
	(4)			
C8-N1-C7-C6	-178.9	C21-N2-C20-C19	180.0 (4)	-178.2
	(4)			
C7-N1-C8-C9	-170.7 (4)	C20-N2-C21-C22	171.0 (4)	-169.3

calculations are accepted as a base to calculate other properties or to evaluate some characteristics for the studied compound.

Vibrational spectral analysis

The two benzene rings of the studied molecule are not absolutely planar with torsion angle of about $10.4(4)^{\circ}$, and the molecular structure belongs to C_1 point group. The molecule with 27 atoms has 75 normal vibrations. All the fundamental modes with their mode numbers can be obtained by theoretical calculation. According to the motion of the individual atoms with the aid of GaussView 3.0 software [23], the detailed vibrational spectral assignments have been given in Table 3 with theoretical frequencies scaled by the factor of 0.9614 for B3LYP method [40,41].

The IR and Raman spectra of the studied compound are shown in Figs. 2 and 3, respectively. The detailed vibrational analysis is completely given below in the work.

C-H vibrations

The aromatic C—H stretching vibration shows in the region $3100-3000 \text{ cm}^{-1}$, which is a typical vibration region for characterization of the aromatic compounds [42,43]. In the present case, the scaled C—H stretching vibrations region at $3095-3045 \text{ cm}^{-1}$ (mode Nos. 74–66) by B3LYP/6–31G(d) method are in excellent agreement with the FT-IR band observed at 3046 cm^{-1} . In this region, the involvement of the substitution has not much impact on the vibration of the aromatic C—H stretching.

The aromatic C—H in-plane bending vibration occurs in the range of 1290–900 cm⁻¹ and the out-of-plane bending vibration shows in the frequency range of 999–755 cm⁻¹ in the substituted benzene compounds [42,43]. The C—H in-plane bending vibrations computed at 1281–1019 cm⁻¹(mode Nos. 50, 47 and 45–39) by B3LYP/6–31G(d) method are closed to experimental FT-IR wavelengths at 1244, 1161, 1026 cm⁻¹ and 1256, 1143, 1101, 1046, 1030 cm⁻¹ in FT-Raman spectrum. These vibration modes often accompany with the C—C, C—O or C—N vibrations. The FT-IR peaks at 854, 808, 765, 726 cm⁻¹ and FT-Raman spectrum at 738 cm⁻¹ are assigned to C—H out-plane bending vibrations, which also show good agreements with the theoretically scaled values at 943–701 cm⁻¹ (mode Nos. 37–33, 31–29, 27, 25–23).

Ring vibrations

The aromatic ring C=C stretching vibrations generally appear in the special region of 1650–1450 cm⁻¹ [39]. In the present work, the ring C=C stretching vibrations are very prominent. In the studied case, the strong bands observed at 1632, 1613, 1530, 1487, 1463, 1416, 1370 cm⁻¹ in FT-IR and the middle to strong bands at 1526, 1513, 1372, 1358 cm⁻¹ in FT-Raman are assigned to the aromatic C=C stretching vibrations, which are good coherence with theoretically calculated data at 1622–1322 cm⁻¹ (mode Nos. 64–61, 59–54, 52). In general, most of these modes are accompanied with the combination of the C–H in-plane bending vibrations.

The bands observed of 573, 549, 525, 478 and 420 cm⁻¹ in FT-IR spectrum are assigned to C—C—C deformation vibrations of the phenyl rings. The deformation vibrations appear at 631, 582, 544, 477 and 446 cm⁻¹ in FT-Raman spectrum. The theoretically computed C—C—C deformation vibrations have been found to show good agreement with recorded spectral date region.

C-N vibrations

The identification of C—N vibration is a rather difficult task for imine compounds, because the C—N vibrational modes often accompany with the combination of neighboring substructures. However, the C—N vibrational spectral assignments can be identified through the animation application of GaussView 3.0 graphical interface for Gaussian output file. In view of this, a very strong band at 1632 cm^{-1} in FT-IR spectrum and 1627 cm^{-1} in FT-Raman is ascribed to a vibration combined with C=N, C1-O1 and C-C stretching vibrations as well as imine N-H and C-H in-plane bending, which agrees well with the calculated value at 1622 cm^{-1} (mode No. 64). And the theoretically predicted frequency (mode No. 51) at 1290 cm^{-1} is attributed to the C-N stretching vibration with N1-H in-plane bending mode, which also matches the experimental value at 1276 cm^{-1} in FT-IR. All these results are close to the data reported by Ilic et al. [44].

C—O vibrations

In the studied case, the medium band at 1593 cm⁻¹ in FT-IR and the strong band at 1597 cm⁻¹ are ascribed to C1—O1 stretching vibration mixed with imine C—H in-plane bending mode, which agree with the calculated value at 1565 cm⁻¹ (mode No. 60). And the theoretically predicted frequency (mode No. 49) at 1258 cm⁻¹ is ascribed to the C9—O2 stretching vibrational mode mixed with C—H in-plane bending vibrations of the No. 2 ring, which is also matches the experimental medium-strong band of 1224 cm⁻¹ in FT-IR and the medium band of 1308 cm⁻¹ in FT-Raman. We can find that the C—O vibration has been affected by neighboring molecular interactions.

O–H vibrations

The reported in-plane O—H bending leads to a medium to strong band in the region of 1440–1260 cm⁻¹[43]. In this case, The O—H in-plane bending vibration is mixed with other vibrations such as C—H in-plane bending, C—C stretching vibration and C—N stretching vibration. The calculated frequencies at 1328, 1281, 1215, 1181, 1157, 1147 and 1082 cm⁻¹ (mode Nos. 53, 50, 47–44, 41) show slightly deviates from the FT-IR bands at 1307, 1244, 1161, 1140, 1117, 1026 cm⁻¹ and the FI-Raman peaks at 1281, 1256, 1167, 1143, 1101 cm⁻¹. These vibrational modes are designated to O-H in-plane bending vibrations mixed with C7—H, or C—H of No. 1 or No. 2 rings. The O—H and N—H stretching modes exhibit marked differences between experimental and theoretical spectra, which attract us to reveal them explained in Proton transfer analysis.

Proton transfer analysis

For an isolated phenol, the frequency of O—H stretching vibration in the gas phase is at about 3650 cm⁻¹ [45,46]. In this work, the theoretical O—H stretching vibration is also at 3605 cm⁻¹ close to the values reported previously[45,46]. However, the FT-IR spectrum shows obvious abnormal spectral bands in the high region, which indicate the O—H group vibrations are affected by surroundings strongly. As a result, it is a different work to assign the hydrogen-bonding vibrational bands by the old-fashioned way.

In order to reveal these vibrations, we need to research on the atomic positions of hydrogen for the studied compound. As we know that the experimental hydrogen positions cannot be obtained directly by the X-ray diffraction technique, and hydrogen atoms are generally placed to their adjacent parent atoms by a semiempirical theoretical calculation. In the fact, the real atomic positions can be determined by the Q peaks, viz., Fourier differences obtained by X-ray diffraction technique. In other word, the Q peaks can supply the real atomic positions effectively. Based on the viewpoint, we need to research the adjacent Q positions of the N and O atoms to find out the real positions of the hydrogen-bonding atoms. The Q peak positions presented by X-ray diffraction are shown in Fig. 4.

In the packing structure of the studied compound, the real H atomic positions should be close to the Q peaks shown in Fig. 4. According to the Q positions and Hooke's Law for harmonic oscillator, we can assign the experimental FT-IR bands related to the

Table 3

Experimental bands and theoretical frequencies with approximate assignments for HPIMP.^{a,b}

Mode Nos.	Experimental		Theoretical	Theoretical		Approximate assignments		
	IR	Raman	Frep.	I _{IR}	I _{Raman}			
75			3605	51.2	1.5	v02H		
74			3095	19.0	4.0	vCH of R ₂		
73	2010		3091	21.2	3.7	vCH of R ₁		
72	3046w		3088	23.2	2.3	vCH of R		
71			3078	18.1	1.5	vCH of R ₁		
69			3067	1.7	1.4	vC7H		
68			3054	99.7	0.6	vC3H		
67			3048	346.2	1.5	υ C10H		
66			3045	28.8	1.6	υC5H		
65			2938	51.4	0.7	vN1H		
64	1632vs	1627s	1622	256.2	86.5	$vC = C \text{ of } R_1 + vC7N1 + vC101 + \beta N1H + \beta C7H$		
63	1612m		1616	17.2	92.6	$vv C = C \text{ of } R_1 + vC/NI + \beta NIH$		
61	1015111		1583	14.6	45	$\nu C = C \text{ of } R_2$		
60	1593m	1597s	1565	105.7	98.1	$vC101 + \beta N1H$		
59	1530s	1526m	1496	27.9	20.4	$vC = C \text{ of } R_1$		
58	1487m		1486	68.4	5.0	$vC = C \text{ of } R_2 + \beta CH \text{ of } R_2$		
57	1463vs	1513m	1454	75.1	49.2	$vC = C \text{ of } R_2 + \beta CH \text{ of } R_2$		
56			1444	30.7	4.1	$vC = C \text{ of } R_1 + \beta CH \text{ of } R_1$		
55	1416w	1272	1409	53.7	7.9	$vC = C \text{ of } R_1 + \beta CH \text{ of } R_1$		
54 52	13/UW 1207m	13/2ms	1301	14.5	10.2	$\beta C = C \text{ of } R_1 + \beta C H \text{ of } R_1$		
52	150/11	1358vc	1320	33.0	2.5	$pC = C \text{ of } \mathbf{R}_1 + \beta C H \text{ of } \mathbf{R}_2 + \beta C 2 H + \beta C 7 H$		
51	1276ms	133083	1290	82.3	0.8	pC7N1 + gN1H		
50	1244s		1281	21.5	0.7	β CH of R ₂ + β O2H		
49	1224ms	1308m	1258	29.1	18.6	ν C902 + β CH of R ₂		
48		1281m	1231	4.1	3.2	β C7H + β N1H + β C5H		
47	1161w	1256ms	1215	15.2	24.9	β CH of R ₁ + β O2H + ν N1C8		
46	1140vs	1167m	1181	181.3	53.9	β O2H + β N1H + v N1C8 + β CH of R ₁		
45	1117w		1157	23.9	0.7	β O2H + β CH of R ₂		
44		1143s	1147	2.4	5.0	β O2H + β CH of R ₂		
43			1142	26.0	3.9	β CH of R ₁		
42	10264	1101m	1003	7.1	0.2	$\beta CH OI R_1 + 0 C - C OI R_1$		
40	102000	1046m	1032	3.8	2.0	$\nu C_{11}C_{12} + \beta C_{11}C_{12} + \beta C_{11}C_{12}$		
39		1040m	1019	3.2	6.3	ν C3C4 + β CH of R ₁		
38	904w		964	9.5	6.4	γ C7H + γ N1H		
37			943	0.3	0.0	γ CH of R ₁		
36			924	0.0	0.2	γCH of R ₂		
35			903	0.9	0.6	γ CH of R ₁		
34			893	6.7	1.7	αR_1		
33	854vw	050-	880	15.7	0.7	γ CH of R ₂		
32		850s	842	8.0	3.0	$\gamma C/H + \gamma N IH$		
30	8081/14/		815	3.6	0.8	$\gamma CH OI R_1 + \alpha R_2 + 0 NICo$ $\alpha R_0 + \nu NICO + \nu CH of R_2$		
29	765m		802	72.8	1.1	vCH of R ₂		
28		772s	797	23.9	11.7	αR_2		
27			755	5.3	1.0	γCH of $R_1 + \nu R_1$		
26	743m		738	74.3	1.0	vC1C6		
25	726w	738w	729	38.9	4.1	γ CH of R ₂		
24			717	4.7	0.3	γ CH of R ₁		
23	F72	C21	701	0.4	0.2	$vR_2 + \gamma CH \text{ of } R_2$		
22	573W	592m	572	5.5 11.4	2.1	$\alpha R_1 + \alpha R_2$		
20	J45III	562111	564	3.2	0.5	$\alpha R_1 + \alpha R_2$ $\alpha R_1 + \alpha R_2$		
19			553	1.5	0.3	vRa		
18			534	0.7	0.5	$\alpha R_1 + \alpha C8C9O2$		
17	525vw	544w	522	1.6	1.9	vR ₁		
16	478m		496	6.6	1.9	$\alpha R_2 + \eta C1O1$		
15		477m	476	2.9	10.8	$\alpha R_1 + \alpha R_2 + \eta C1O1$		
14			442	4.1	0.4	$vR_1 + vR_2$		
13	420	446W	434	5.0	3.2	$vK_1 + vK_2$		
12	420W	3420	407	3.1 107 1	1.0 2.1	$\eta \cup 9 \cup 2 + \alpha \cup 2 \cup \cup 1$ $\eta \cup 1 \cup 1 + \eta \cup 2 \cup 1$		
10		3425	330	57	2.1	nO2H		
9		295vw	303	03	24.0	nO2H		
- 8		242w	251	3.7	1.6	ηC902		
7			216	0.7	2.5	ρSkeleton		
6		214m	205	1.6	28.7	hoSkeleton		
5		182vw	180	1.4	9.6	hoSkeleton		
4		145vw	131	0.3	38.1	hoSkeleton		
3			68	0.4	32.4	ωSkeleton		

Table J (continued)	Table 3	(continued)	
---------------------	---------	-------------	--

Mode Nos.	Experimental		Theoretical			Approximate assignments	
	IR	Raman	Frep.	$I_{\rm IR}$	I _{Raman}		
2			54	1.2	46.7	ω Skeleton	
1			32	0.9	369.2	auSkeleton	

^a Mode numbers are extracted from the output result of the B3LYP calculation;

^b B3LYP scaled wavenumbers (m^{-1}). The calculated IR intensities (I_{IR}) are in k mmol⁻¹; the calculated Raman scattering intensities (I_{Raman}) are in arbitrary units by Eq. (1); s, strong; vs. very strong; m, medium; ms, medium strong; w, weak; vw, very weak; b, broad; R, ring (R₁: C1~C6, R₂: C8~C13); α , angle bending; β , in-plane bending; γ , outof-plane bending; ν , puckering; ω , wagging; ν , stretching, τ , torsion, η , nodding.



Fig. 3. The Raman of HPIMP: (a) recorded (b) simulated.



Fig. 4. The Q positions related to hydrogen-bonding interaction in packing HPIMP.

hydrogen-bonding atoms. The broad band at 2856, 2699 cm⁻¹ are respectively ascribed to the stretching vibration of the phenolic hydroxyl and imine groups. While the broad band at 2575 cm⁻¹ is designated to the mixed O1—H and O4—H stretching mode owing to the intermolecular hydrogen bonding interaction.

 Table 4

 The thermodynamic properties at different temperatures for HPIMP.

Temperature (K)	$C_{p,m}^{\Theta}$ (J/mol/K)	S_m^{Θ} (J/mol/K)	ΔH_m^{Θ} (kJ/mol)
100.0	89.97	329.36	6.13
200.0	159.45	412.33	18.50
298.1	233.08	489.75	37.77
400.0	302.69	568.25	65.15
500.0	358.86	642.06	98.33
600.0	403.55	711.59	136.54
700.0	439.22	776.57	178.74
800.0	468.16	837.17	224.16

Based on the detailed investigation on the hydrogen-bonding spectral bands and X-ray Q peaks of the N and O atoms, we can further draw a mechanism of the intramolecular and intermolecular proton transfer procedures for the studied compound (Scheme 2). Accompany with resonance, the intramolecular proton exchange effect leads to the keto-enol conversion between the phenolate and phenol configurations, while the intermolecular proton transfer effect brings out the positive and negative molecules.

The three abnormal spectral bands observed in high region are ascribed to the strong intramolecular and intermolecular effects,



Scheme 2. Intramolecular and intermolecular proton transfer procedures of HPIMP^a. ^a Dash lines indicate hydrogen bonding.

Table 5					
The calculated electric dipole moments	(Debye), static polarizability	components (a.u.), first	t hyperpolarizability	components (a.u.)	of HPIMP.

μ_x	μ_y	μ_z	α _{xx}	α_{yy}	α _{zz}	β_{XXX}	β_{xxy}	β_{xyy}	β_{yyy}	β_{xxz}	β_{yyz}	β_{xzz}	β_{yzz}	β_{zzz}
-1.43	-0.77	-0.15	322.33	159.26	50.96	649.76	-431.53	22.92	-91.45	-25.64	9.25	2.73	-5.38	-0.92

which supply a clear experimental proof for the proton transfer mechanism. Based on the breakthrough, the variable structures of the studied molecule can be obtained by the interpretation on the proton transfer procedure.

We can find that the strong hydrogen bonds have great effect on the stretching modes of the hydrogen-bonding-related atoms. The IR and X-ray techniques provide an excellent approach for us to study the strong interactions. The vibrational spectral characteristics in high region and X-ray Q peaks supply important experimental evidences to research on the proton-transfer interaction in medicine, life, material fields. The proton transfer analysis in this work provides a good demonstration to study long-range proton transfer processes.

Thermodynamic properties

On the basis of vibrational frequencies gained at B3LYP/6-31G(d) level and statistical thermodynamic parameters: heat capacities ($C_{p,m}^{\Theta}$), entropies (S_m^{Θ}) and enthalpies (ΔH_m^{Θ}) can be obtained from the theoretical frequencies scaled by 0.9614. And the values of the thermodynamic functions at different temperatures are listed in Table 4.

As is an evidence from Table 5, all the values of heat capacities $(C_{p,m}^{\Theta})$, entropies (S_m^{Θ}) and enthalpies (ΔH_m^{Θ}) increase with temperature ranging from 100.0 to 800.0 K due to the enhancement of the molecular vibration with the increasing temperature. The correlative equations between the thermodynamic properties and temperatures were fitted by quadratic formulas, and the corresponding correlation coefficients are all beyond 0.999. The correlation graphics shows in Fig. 5 and the corresponding fitting equations are as follows:

$$C_{p,m}^{\Theta} = -3.8694 + 0.9324T - 4.2625 \times 10^{-4} T^2$$
(5)

$$S_m^{\Theta} = 241.4318 + 0.8911T - 1.8184 \times 10^{-4}T^2$$
(6)

$$\Delta H_m^{\Theta} = -4.8039 + 0.0657T + 2.7828 \times 10^{-4} T^2 \tag{7}$$

All the thermodynamic data provide helpful information to further study on the title compound in the thermodynamic field.

NLO behavior

It is an important and inexpensive way to evaluate the NLO properties of materials by theoretical calculations. To understand the microscopic NLO mechanism of the title compound, we have applied Gaussian 03W program [22] to calculate electric dipole moment components, static polarizability components and first hyperpolarizability components. All the calculated results were listed in Table 5. And the dipole polarizability μ_0 , the average linear polarizability α_0 and the first-order hyperpolarizability β_0 can be calculated by the formula (2)–(4). The corresponding values of μ_0 , α_0 and β_0 are 1.63 Debye, 26.28 Å³ and 7.41 × 10⁻³⁰ cm⁵/esu, respectively. The α_0 and β_0 value of the investigated compound are all higher than those of urea ($\alpha_0 = 3.83 Å^3$, $\beta_0 = 3.73 \times 10^{-31} \text{ cm}^5$ /esu). Especially, the first-order hyperpolarizability value of the investigated compound is 19.9 times more than that of urea, which is also larger than several reported values [3,34,37,47,48].



Fig. 5. The correlation graphics of thermodynamic functions via temperatures for HPIMP.

That is to say, the compound probably is also a good candidate of NLO materials.

Conclusions

Determinations have been made in this present work for the molecular structure and spectral assignments of (*E*)-2-((2-hydroxyphenyl)iminiomethyl)phenolate from single crystal XRD, FT-IR and FT-Raman spectra with the aid of the theoretical calculations at B3LYP/6-31G(d) level. The experimental and theoretical results support well each other. Three abnormal spectral bands can be explained by the X-ray diffraction Q peak positions of adjacent N and O atoms, and the bands and Q peaks also supply good experimental evidences to reveal the proton transfer procedures for the studied compound. In addition, the thermodynamic and NLO properties for the compound have been given by theoretical calculations. The theoretical higher hyperpolarizability values imply that the title compound might become a kind of good NLO material.

Acknowledgments

This work was supported by Natural Science Foundations of China (No. 21073092 & 21103092), Sichuan Education Department Fund (No. 12ZA080), Scientific Research Foundation for Excellent Plan of Binzhou University (BZXYQNLG200704) and Excellent Plan Foundation of NUST (2008). We also thank Qufu Normal University for Technical Assistance.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.04.094.

References

- [1] H. Ünver, A. Karakas, A. Elmali, J. Mol. Struct. 702 (2004) 49-54.
- [2] A. Karakas, H. Ünver, Spectrochim. Acta A 75 (2010) 1492–1496.
- [3] Y. Sun, Q. Hao, W. Wei, Z. Yu, L. Lu, X. Wang, Y. Wang, J. Mol. Struct.: THEOCHEM 904 (2009) 74–82.
- [4] Y. Sun, Q. Hao, Z. Yu, W. Wei, L. Lu, X. Wang, Mol. Phys. 107 (2009) 223–235.
- [5] Y. Sun, Q. Hao, W. Wei, Z. Yu, L. Lu, X. Wang, Y. Wang, J. Mol. Struct. 929 (2009) 10–21.
- [6] Y. Sun, W. Wei, Q. Hao, L. Lu, X. Wang, Spectrochim. Acta A 73 (2009) 772-781.
- [7] H. Ünver, A. Karakaş, A. Elmali, T.N. Durlu, J. Mol. Struct. 737 (2005) 131-137.
- [8] E. Hadjoudis, M. Vittorakis, I. Moustakali-Mavridis, Tetrahedron 43 (1987)
- 1345–1360. [9] H. Ünver, T. Nuri Durlu, J. Mol. Struct. 655 (2003) 369–374.
- [10] A.N. Bondar, S. Suhai, S. Fischer, J.C. Smith, M. Elstner, J. Struct. Biol. 157 (2007) 454-469
- [11] A. Filarowski, A. Koll, A. Karpfen, P. Wolschann, Chem. Phys. 297 (2004) 323-332.
- [12] H. Tanak, A.A. Ağar, O. Büyükgüngör, Spectrochim. Acta A 87 (2012) 15-24.
- [13] R.R.B.N.K. Sethuraman, Spectrochim. Acta A 66 (2007) 707-711.
- [14] Y. Wang, Z. Yu, Y. Sun, Y. Wang, L. Lu, Spectrochim. Acta A 79 (2011) 1475– 1482.
- [15] J.J. Li, Pomeranz–Fritsch reaction, Springer, Berlin Heidelberg, New York, 2006. pp. 472–474.
- [16] J.L. Chambers, K.L. Smith, M.R. Pressprich, Z. Jin, SMART, Bruker Advanced Xray Solutions, Version 5.628., Bruker AXS Inc. Madison, WI, 2002.
- [17] SAINTPlus, Data Reduction and Correction Program, Version 6.22., Bruker AXS Inc. Madison. WI. 2001.
- [18] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Dectector Data, University of Gottingen, Germany, 1996.
- [19] G.M. Sheldrick, SHELXS-97 and SHELXL-97; Programs for Structure Resolution
- and for Structure Refinement, University of Gottingen, Germany, 1997. [20] G.M. Sheldrick, SHELXTL, Structure Determination Software Suite, Version
- 6.10., Bruker AXS Inc. Madison, WI, 2000. [21] H. Arslan, O. Algul, T. Onkol, Spectrochim. Acta A 70 (2008) 606–614.
- [22] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar,

J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03W, Version 6.0., Gaussian, Inc. Wallingford CT, 2004.

- [23] R. Dennington II, T. Keith, J. Millam, K. Eppinnett, W. Lee Hovell, R. Gilliland, GaussView, Version 3.09., Semichem, Inc. Shawnee Mission, KS, 2003.
- [24] V. Krishnakumar, G. Keresztury, T. Sundius, R. Ramasamy, J. Mol. Struct. 702 (2004) 9–21.
- [25] P.L. Polavarapu, J. Phys. Chem. 94 (1990) 8106-8112.
- [26] R. Zhang, B. Du, G. Sun, Y. Sun, Spectrochim. Acta A 75 (2010) 1115-1124.
- [27] A. Karakas, A. Elmali, H. Ünver, I. Svoboda, Spectrochim. Acta A 61 (2005) 2979–2987.
- [28] P.S. Liyanage, R.M. de Silva, K.M.N. de Silva, J. Mol. Struct.: THEOCHEM 639 (2003) 195-201.
- [29] P.J. Mendes, J.P.P. Ramalho, A.J.E. Candeias, M.P. Robalo, M.H. Garcia, J. Mol. Struct.: THEOCHEM 729 (2005) 109–113.
- [30] I.C. de Silva, R.M. de Silva, K.M. Nalin De Silva, J Mol Struc: THEOCHEM 728 (2005) 141-145.
- [31] J.O. Morley, J. Am. Chem. Soc. 110 (1988) 7660-7663.
- [32] H. Li, K. Han, X. Shen, Z. Lu, Z. Huang, W. Zhang, Z. Zhang, L. Bai, J. Mol. Struct.: THEOCHEM 767 (2006) 113–118.
- [33] A.D. Tillekaratne, R.M. de Silva, K.M.N. de Silva, J. Mol. Struct.: THEOCHEM 638 (2003) 169-176.
- [34] D. Sajan, H. Joe, V.S. Jayakumar, J. Zaleski, J. Mol. Struct. 785 (2006) 43-53.
- [35] H. Alyar, Z. Kantarci, M. Bahat, E. Kasap, J. Mol. Struct 2007 (2007) 516-520.
- [36] N. Sundaraganesan, J. Karpagam, S. Sebastian, J.P. Cornard, Spectrochim. Acta A 73 (2009) 11–19.
- [37] K.S. Thanthiriwatte, K.M. Nalin de Silva, J. Mol. Struct.: THEOCHEM 617 (2002) 169–175.
- [38] A.K. Mukherjee, R.L. De, I. Banerjee, C. Samanta, N.P. Nayak, Acta Crystallogr. Sect. C 55 (1999) 407–410.
- [39] M. Karabacak, E. Şahin, M. Çınar, I. Erol, M. Kurt, J. Mol. Struct. 886 (2008) 148– 157.
- [40] A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502-16513.
- [41] I.M. Alecu, J. Zheng, Y. Zhao, D.G. Truhlar, J. Chem. Theory Compu. 6 (2010) 2872-2887.
- [42] J. Swaminathan, M. Ramalingam, V. Sethuraman, N. Sundaraganesan, S. Sebastian, Spectrochim. Acta A 73 (2009) 593–600.
- [43] L. Guru Prasad, V. Krishnakumar, R. Nagalakshmi, Physica B 405 (2010) 1652– 1657.
- [44] M. Ilic, E. Koglin, A. Pohlmeier, H.D. Narres, M.J. Schwuger, Langmuir 16 (2000) 8946-8951.
- [45] D. Michalska, D.C. Bienko, A.J. Abkowicz-Bienko, Z. Latajka, J. Phys. Chem. 100 (1996) 17786–17790.
- [46] G.V. Hartland, B.F. Henson, V.A. Venturo, P.M. Felker, J. Phys. Chem. 96 (1992) 1164–1173.
- [47] C. Ravikumar, I.H. Joe, V.S. Jayakumar, Chem. Phys. Lett. 460 (2008) 552-558.
- [48] F.F. Jian, P. Zhao, L. Zhang, J. Zheng, J. Fluo. Chem. 127 (2006) 63-67.