



Theoretical and experimental vibrational spectrum study of 4-hydroxybenzoic acid as monomer and dimer

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ABSTRACT

Theoretical calculations on the molecular geometry and the vibrational spectrum of 4-hydroxybenzoic acid were carried out by the Density Functional Theory (DFT/B3LYP) method. In addition, IR and Raman spectra of the 4-hydroxybenzoic acid in solid phase were newly recorded using them in conjunction the experimental and theoretical data (including SQM calculations), a vibrational analysis of this molecular specie was accomplished and a reassignment of the normal modes corresponding to some spectral bands was proposed. The geometries of monomers and dimers in gas phase were optimized using the DFT B3LYP method with the 6-31G*, D95** and 6-311++G** basis sets. Also, both the vibrational spectra recorded and the results of the theoretical calculations show the presence of one stable conformer for the 4-hydroxybenzoic acid cyclic dimer. The B3LYP/6-31G* method was used to study the structure for cyclic dimer of 4-hydroxybenzoic acid and for a complete assignment our results were compared with results of the cyclic dimer of benzoic acid. A scaled quantum mechanical analysis was carried out to yield the best set of harmonic force constants. The formation of the hydrogen bond was investigated in terms of the charge density by the AIM program and by the NBO calculations.

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1. Introduction

The 4-hydroxybenzoic acid is the simplest of the three components of the hydroxybenzoic series of the so named “polyphenols” belonging to the group of the minor constituents of olive oil, chemically unrelated with fatty acids [1]. The cell antioxidant action in living organisms, and especially in humans, of this type of compounds has been amply proved [2–4]. Hence, at present their bio-medical interest is clearly increasing for the prevention and treatment of cell ageing [5–7] and cardiovascular [8,9] and carcinogenic diseases [10–16], etc. In addition, the 4-hydroxybenzoic acid and some of their derivatives are of high industrial interest when preparing synthetic high polymers to be used in novel liquid crystals [17–20]. We think that a more thorough and better knowledge of the structural properties and of spectroscopic characteristics of this and other similar molecular species could help significantly form to get major advances in the above referred applications.

At this time, only a few references relative to the molecular structure [21–26], electronic structure and thermodynamic properties [27,28] and vibrational spectra of 4-hydroxybenzoic acid appear in the literature [22,29–31]. Thus, in 1986 Sánchez de La

Blanca et al. [30,31] carried out an incomplete assignment of its vibrational spectrum by recording its IR and Raman spectra and with the help of group theory. In this way, they were able to assign 31 of the 42 vibrational normal modes expected for this molecule. From their results they proposed that the 4-hydroxybenzoic acid solid has intermolecular hydrogen bond. Later, a theoretical study of the structures and of the hydrogen bonds in the gas phase (*ab initio* quantum chemical calculations) and aqueous solution (Monte Carlo simulations for isothermal–isobaric ensembles) of the 2- and 4-hydroxybenzoic acids was realized by Nagy et al. [22]. In this last case the authors using the MP2 method with the basis set 6-31G*, accomplished a total geometry optimization of eight and four, theoretically possible planar conformers in phase gas respectively for the hydroxy-carboxylic derivatives above mentioned. They have also calculated the corresponding fundamental theoretical vibrational frequencies of all those conformers although without trying to carry out any assignment of their corresponding normal modes to the experimental vibrational spectra.

The crystal structure and molecular structural data from the solid phase of 4-hydroxybenzoic acid were firstly given by Colapietro et al. [24] by using X-ray diffraction. Later, Heath et al. [23] carried out a new experimental study and they showed that two molecules of the acid are linked through hydrogen bonds between their carboxylic groups thus a centre-symmetrical cyclic structure originated for the corresponding dimer. The benzenic ring has essentially hexagonal symmetry being its carbon atoms practically

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coplanar while the hydrogen and oxygen atoms of the hydroxyl and carboxylic groups are only slightly deviated from the ring plane.

In order to get the best possible characterization and identification of the components of the hydroxybenzoic series of the “polyphenols”, in this paper we carried out a more complete and reliable assignment of the vibrational spectra of 4-hydroxybenzoic acid. Thus, we first performed geometry optimization calculations for the monomer and cyclic dimer of 4-hydroxybenzoic acid using DFT/B3LYP methods with 6-31G*, D95** and 6-311++G** basis sets. Later, in order to assure a correct assignment of the experimental (IR and Raman) spectra of this molecule to its corresponding vibrational normal modes, we accomplished a theoretical/experimental analysis of vibrational spectra. Besides, calculations of the force constant associated to the main normal modes of vibration and the potential energy distribution with the scaled quantum mechanics (SQM) force field were performed. The total energies calculated with all basis sets for 4-hydroxybenzoic acid cyclic dimer were corrected for basis set superposition error (BSSE) by the standard Boys–Bernardi counterpoise method [32].

In addition, the frequency bands in the vibrational spectra of 4-hydroxybenzoic acid in solid phase could be supported with the theoretical calculations for the centrosymmetric dimeric species and with other papers reported in the literature for benzoic acid cyclic dimer [33–41] and *o*-hydroxybenzoic acid [42]. The topological AIM charge density analysis [43–45] and the NBO studies [46–49] for dimeric species show a characteristic structure of the OH stretching band typically associated with strong hydrogen bonds.

2. Experimental details

The 4-hydroxybenzoic acid was obtained from Sigma–Aldrich (99%) and was used without any further purification. The infrared spectra of the solid sample in KBr pellets at room temperature, in the range between 4000 and 400 cm⁻¹ and with 1 cm⁻¹ of resolution were registered on a Perkin Elmer 1760-X FTIR spectrophotometer. In addition, the Raman spectra of the solid samples, in the range between 4000 and 50 cm⁻¹ and with a resolution of 1 cm⁻¹, were also registered at room temperature on a FT-Raman RF100/S Bruker spectrometer, using light of 1064 nm from an Nd/YAG laser for excitation.

3. Computational details

Initial structures for 4-hydroxybenzoic acid monomer and cyclic dimer were modelled with the GaussView Program [50] using Density Functional Theory. All the calculations were made using the GAUSSIAN 03 program [51] running on a Digital Alpha Server 4100. In vibrational studies of the benzoic acid monomer and dimer, various authors have examined the basis set dependence on the structural parameters and the infrared spectrum [34–39]. Hence, we have performed calculations for the geometries and harmonic frequencies in cartesian coordinates of monomer and cyclic dimer of 4-hydroxybenzoic acid using 6-31G*, D95** [52,53] and 6-311+G* basis sets. The resulting force field calculations were transformed to “natural” internal coordinates by the MOLVIB program [54,55]. The natural coordinates for 4-hydroxybenzoic acid monomer are shown in Table S1 of the Supporting Material and have been defined as proposed by Fogarasi and Pulay [56] and the definition of internal coordinates used is observed in Fig. 1. The natural coordinates for the cyclic dimer are the same as in the monomer for molecule in Fig. 1 following numeration of atoms from 17 to 32, as indicated in Fig. 2. Table S2 shows only the six intermonomer coordinates for the cyclic dimer, which are simi-

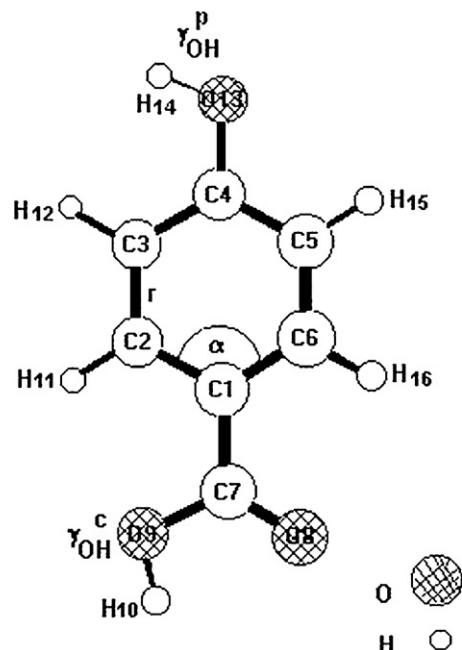


Fig. 1. Definition of internal coordinates for monomers of 4-hydroxybenzoic acid.

lar to those, defined by other authors for the benzoic acid dimer [36,37,39].

The force field was scaled using the transferable scale factors of Rauhut and Pulay [57–59] with the MOLVIB program. The potential energy distribution (PED) components greater than or equal to 10% are subsequently calculated with the resulting scaled quantum mechanics (SQM) force field.

The main stabilization energies were calculated by means of the Natural Bond Orbital (NBO) approach [46–49], as implemented in the GAUSSIAN 03 package, using the B3LYP/6-311++G** method. Moreover, at the same level of calculation the topological properties of the charge density for the cyclic dimer were computed by means of the AIM2000 program [44]. The total energies for cyclic dimers were corrected for basis set superposition error (BSSE) by the standard Boys–Bernardi counterpoise method [32].

4. Results and discussion

4.1. Geometry

The DFT calculations show the presence of four conformers of 4-hydroxybenzoic acid monomer, but only I and II conformers are stable (see Fig. 2), in accordance with the MP2 calculations by Nagy et al. [22]. The optimized geometries using B3LYP method with 6-31G*, D95** and 6-311+G* basis sets are observed in Table S3 and are compared with those experimental values obtained by Colapietro et al. [24]. We observed that the geometrical parameters of the monomer species using B3LYP method are not better than those obtained for Nagy et al. [22]. Obviously, the optimized bond lengths are longer than the experimental values because in the first case the calculations were carried out with the isolated molecules in gas phase whereas in the second one they were performed in solid phase.

For the calculations of the cyclic dimer we considered two structures, form I with the phenolic OH in the same position and form II in different position, as shown in Fig. 3. In all cases, planar structures for both monomers and cyclic dimer are predicted. The optimized structures with 6-31G*, D95** and 6-311+G* basis sets for two monomer species have C₁ symmetry whereas for cyclic dimer, I

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