

Energetics of Hydroxybenzoic Acids and of the Corresponding Carboxyphenoxy Radicals. Intramolecular Hydrogen Bonding in 2-Hydroxybenzoic Acid

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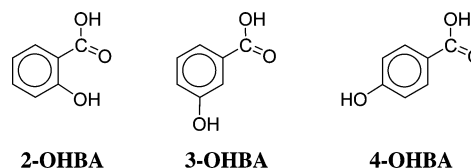
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Received: July 29, 2005

The energetics of the phenolic O–H bond in the three hydroxybenzoic acid isomers and of the intramolecular hydrogen O–H...O–C bond in 2-hydroxybenzoic acid, 2-OHBA, were investigated by using a combination of experimental and theoretical methods. The standard molar enthalpies of formation of monoclinic 3- and 4-hydroxybenzoic acids, at 298.15 K, were determined as $\Delta_f H_m^o(3\text{-OHBA, cr}) = -593.9 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H_m^o(4\text{-OHBA, cr}) = -597.2 \pm 1.4 \text{ kJ}\cdot\text{mol}^{-1}$, by combustion calorimetry. Calvet drop-sublimation calorimetric measurements on monoclinic samples of 2-, 3-, and 4-OHBA, led to the following enthalpy of sublimation values at 298.15 K: $\Delta_{\text{sub}} H_m^o(2\text{-OHBA}) = 94.4 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_{\text{sub}} H_m^o(3\text{-OHBA}) = 118.3 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$, and $\Delta_{\text{sub}} H_m^o(4\text{-OHBA}) = 117.0 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$. From the obtained $\Delta_f H_m^o(\text{cr})$ and $\Delta_{\text{sub}} H_m^o$ values and the previously reported enthalpy of formation of monoclinic 2-OHBA ($-591.7 \pm 1.3 \text{ kJ}\cdot\text{mol}^{-1}$), it was possible to derive $\Delta_f H_m^o(2\text{-OHBA, g}) = -497.3 \pm 1.4 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^o(3\text{-OHBA, g}) = -475.6 \pm 2.3 \text{ kJ}\cdot\text{mol}^{-1}$, and $\Delta_f H_m^o(4\text{-OHBA, cr}) = -480.2 \pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$. These values, together with the enthalpies of isodesmic and isogyric gas-phase reactions predicted by density functional theory (B3PW91/aug-cc-pVDZ, MPW1PW91/aug-cc-pVDZ, and MPW1PW91/aug-cc-pVTZ) and the CBS-QMPW1 methods, were used to derive the enthalpies of formation of the gaseous 2-, 3-, and 4-carboxyphenoxy radicals as $\Delta_f H_m^o(2\text{-HOCC}_6\text{H}_4\text{O}^\bullet, \text{g}) = -322.5 \pm 3.0 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^o(3\text{-HOCC}_6\text{H}_4\text{O}^\bullet, \text{g}) = -310.0 \pm 3.0 \text{ kJ}\cdot\text{mol}^{-1}$, and $\Delta_f H_m^o(4\text{-HOCC}_6\text{H}_4\text{O}^\bullet, \text{g}) = -318.2 \pm 3.0 \text{ kJ}\cdot\text{mol}^{-1}$. The O–H bond dissociation enthalpies in 2-OHBA, 3-OHBA, and 4-OHBA were 392.8 ± 3.3 , 383.6 ± 3.8 , and $380.0 \pm 3.4 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. Finally, by using the ortho–para method, it was found that the H...O intramolecular hydrogen bond in the 2-carboxyphenoxy radical is $25.7 \text{ kJ}\cdot\text{mol}^{-1}$, which is ca. $6\text{--}9 \text{ kJ}\cdot\text{mol}^{-1}$ above the one estimated in its parent (2-OHBA), viz. $20.2 \text{ kJ}\cdot\text{mol}^{-1}$ (theoretical) or $17.1 \pm 2.1 \text{ kJ}\cdot\text{mol}^{-1}$ (experimental).

Introduction

The energetics of the three hydroxybenzoic acid isomers (2-, 3-, and 4-OHBA) is at the heart of a variety of fundamental studies, such as the determination of Hammett σ parameters¹ and the experimental^{2–4} and theoretical^{5–8} investigation of hydrogen bonding.^{9–11} It has also significant industrial relevance, because these compounds are used, for example, in the manufacture of pharmaceuticals, pesticides, dyes, agrochemicals, and perfumery products.^{12,13}



We have recently used a combination of experimental and computational chemistry methods to investigate the energetics of organic molecules and radicals through isodesmic reaction schemes.^{14,15} The study of the hydroxybenzoic acid isomers is particularly interesting in this regard, because the “group balance” that leads to the cancellation of errors in the computational prediction of the enthalpies of gas phase isodesmic reactions is not truly possible in the case of 2-OHBA, due to

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the presence of an O—H...O=C intramolecular hydrogen bond (hereafter abbreviated as H-bond). Moreover, the energetics of this bond is still under debate due, essentially, to the considerable discrepancies between the reported experimental values of enthalpies of formation in the crystalline state, $\Delta_f H_m^o(\text{cr})$, and enthalpies of sublimation, $\Delta_{\text{sub}} H_m^o$, of the three acids. The nine published values of the enthalpy of formation of 2-hydroxybenzoic acid (2-OHBA) in the crystalline state span a range of $8.4 \text{ kJ}\cdot\text{mol}^{-1}$,^{3,4,16–24} the two reported $\Delta_f H_m^o(\text{cr})$ values for 3-hydroxybenzoic acid (3-OHBA) show an inconsistency of $3.7 \text{ kJ}\cdot\text{mol}^{-1}$,^{3,4} and the two corresponding values for 4-hydroxybenzoic acid (4-OHBA) differ by $12.2 \text{ kJ}\cdot\text{mol}^{-1}$.^{3,4} Analogous differences are found for the sublimation enthalpy data,^{2–4,25–27} raising serious doubts about the accuracy of the $\Delta_f H_m^o(\text{g})$ values derived from the corresponding $\Delta_f H_m^o(\text{cr})$ and $\Delta_{\text{sub}} H_m^o$ and, therefore, on any conclusions drawn from them. For example, though a stabilization effect of $22.8 \pm 1.8 \text{ kJ}\cdot\text{mol}^{-1}$ due to intramolecular H-bonding is predicted for 2-hydroxybenzoic acid, by comparing the experimental $\Delta_f H_m^o(\text{g})$ result obtained by Colomina et al. ($-493.2 \pm 1.3 \text{ kJ}\cdot\text{mol}^{-1}$, see discussion below)³ with that predicted by a group contribution scheme ($-470.4 \pm 1.2 \text{ kJ}\cdot\text{mol}^{-1}$),²⁸ a much smaller effect ($3.3 \text{ kJ}\cdot\text{mol}^{-1}$) is observed if the difference in enthalpies of formation for gaseous 2-OHBA and 4-OHBA reported by Sabbah et al. ($-496.0 \pm 1.9 \text{ kJ}\cdot\text{mol}^{-1}$ and $-492.7 \pm 2.7 \text{ kJ}\cdot\text{mol}^{-1}$, respectively)⁴ is considered.

The origin of the inconsistencies mentioned above is difficult to ascertain. They may be due, at least in part, to the fact that different polymorphs or mixtures of phases were used in some of the reported studies. It is now well-known that the hydroxy derivatives of benzoic acid exhibit polymorphism,^{19,29–31} and indeed, we recently observed that routine purification of a commercial sample of 2-hydroxybenzoic acid by sublimation and/or simple recrystallization from water did not yield a single phase material.¹⁶

In this work the re-determination of $\Delta_f H_m^o(\text{cr})$, $\Delta_{\text{sub}} H_m^o$, and $\Delta_f H_m^o(\text{g})$ for the complete series of hydroxybenzoic acid isomers was undertaken, based on calorimetric studies of single phase (monoclinic) samples, characterized by X-ray diffraction. The results were then used to assess the theoretical predictions for the enthalpies of a series of isodesmic reactions involving 2-, 3-, and 4-OHBA and to derive the phenolic O—H bond dissociation enthalpies in these compounds. Finally, the intramolecular H-bond in 2-OHBA was discussed on the basis of the recently proposed ortho—para method.³²

Experimental Section

General Information. Elemental analyses were carried out with a Fisons Instruments EA1108 apparatus. The infrared spectra were recorded in a JASCO 430 Fourier transform spectrophotometer, calibrated with polystyrene film, using KBr disks. The ¹H NMR spectra were obtained at ambient temperature in a Varian 300 MHz spectrometer. X-ray powder diffractometry (XRD) was carried out over the range $5^\circ < 2\theta < 40^\circ$, on a Philips PW1710 apparatus employing Cu K α radiation. The powder patterns were indexed using the Checkcell program.³³

Materials. The monoclinic 2-hydroxybenzoic acid sample was that previously used in the determination of $\Delta_f H_m^o(2\text{-OHBA,cr})$.¹⁶ Single phase 3-OHBA was prepared as follows. Approximately 50 g of the acid (Aldrich; mass fraction >0.99) was dissolved in acetonitrile at 307.15 K and filtered into a double-walled vessel whose temperature was controlled

to $\pm 0.1 \text{ K}$ by circulating water from a Julabo F25-EC temperature controller through the double wall. The temperature of the solution was first raised to 310 K and then decreased to 275 K at a rate of $5 \text{ K}\cdot\text{h}^{-1}$. The precipitated 3-hydroxybenzoic acid was separated from the mother liquor by vacuum filtration and dried in an oven for 2 h at 400 K. Elemental analysis for C₇H₆O₃: expected C 60.87%, H 4.38%; found C 60.74%, H 4.39% (average of two determinations). ¹H NMR (300 MHz, CDCl₃/TMS): $\delta = 7.57$ (d,q, CH, 1H), 7.54 (m, CH, 1H), 7.42 (t, CH, 1H), 7.13 (m, CH, 1H). The powder pattern was indexed as monoclinic, space group $P2_1/b$, with $a = 550.3(2) \text{ pm}$, $b = 2392.9(5) \text{ pm}$, $c = 496.0(1) \text{ pm}$, $\gamma = 105.67^\circ$. These results are in excellent agreement with those previously obtained by single-crystal X-ray diffraction for form I of 3-OHBA, $P2_1/b$, $a = 549.3(2)$, $b = 2389.3(9)$, $c = 494.3(2)$, $\gamma = 105.70^\circ$.²⁹

The method of preparation of the 4-OHBA sample was identical to that described above for 3-OHBA. Elemental analysis for C₇H₆O₃: expected C 60.87%, H 4.38%; found C 60.64%, H 4.31% (average of two determinations). ¹H NMR (300 MHz, CDCl₃/TMS): $\delta = 7.88$ (quin., CH, 2H), 6.90 (quin., CH, 2H). The powder pattern was indexed as monoclinic, space group $P2_1/a$, with $a = 1845.6(1) \text{ pm}$, $b = 523.2(4) \text{ pm}$, $c = 634.4(8) \text{ pm}$, $\beta = 93.45^\circ$. This clearly indicated that the sample corresponded to form I of 4-OHBA previously characterized by single-crystal X-ray diffraction: $P2_1/a$, $a = 1850.8(7) \text{ pm}$, $b = 522.8(2) \text{ pm}$, $c = 634.2(3) \text{ pm}$, $\beta = 93.22^\circ$.³⁰

The absence of water in all samples was confirmed by Fourier transform infrared spectroscopy.

Differential Scanning Calorimetry (DSC). The differential scanning calorimetry experiments on monoclinic 2-, 3-, and 4-OHBA were made with a temperature-modulated TA Instruments Inc. 2920 MTDSC apparatus, operated as a conventional DSC. The samples with masses in the range 3.1–6.4 mg, were sealed under air, in aluminum pans, and weighed with a precision of 10^{-7} g in a Mettler UMT2 ultra-micro balance. Helium (Air Liquide N55), at a flow rate of $0.5 \text{ cm}^3\cdot\text{s}^{-1}$, was used as the purging gas. The temperature and heat flow scales of the instrument were calibrated as previously described.³⁴ The heating rate was $1 \text{ K}\cdot\text{min}^{-1}$. No phase transitions were observed in the DSC curves between 298 K and the fusion temperature. The onset and the maximum temperatures of the fusion peaks were 431.8 ± 0.1 and $432.4 \pm 0.1 \text{ K}$ for 2-OHBA, and 475.3 ± 0.1 and $476.35 \pm 0.05 \text{ K}$ for 3-OHBA, respectively. The corresponding enthalpies of fusion were $\Delta_{\text{fus}} H_m^o(2\text{-OHBA}) = 26.1 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_{\text{fus}} H_m^o(3\text{-OHBA}) = 36.5 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$. The uncertainties quoted for T_{fus} and $\Delta_{\text{fus}} H_m^o$ correspond to twice the standard deviation of the mean of five independent determinations. The monoclinic sample of 4-OHBA decomposed on fusion, with the onset at $488.3 \pm 0.1 \text{ K}$. This contrasts with the report of $T_{\text{fus}} = 488.0 \text{ K}$ ³⁵ and $\Delta_{\text{fus}} H_m^o(4\text{-OHBA}) = 30.99 \text{ kJ}\cdot\text{mol}^{-1}$ ³⁵ for 4-OHBA and is in agreement with the observation by Sabbah and Le that 4-OHBA decomposes on fusion with the evolving of CO₂.⁴

Combustion Calorimetry. The isoperibol static-bomb combustion calorimeter used in the determination of the enthalpies of formation of monoclinic 3- and 4-OHBA has been described.¹⁶ The energy equivalent of the apparatus, $\epsilon^\circ = 18\,562.59 \pm 1.84 \text{ J}\cdot\text{K}^{-1}$, was determined from the combustion of benzoic acid (NIST SRM 39j) whose standard massic energy of combustion under the certificate conditions was $\Delta_c u^\circ = -26\,434 \pm 3 \text{ J}\cdot\text{g}^{-1}$. In a typical calorimetric experiment, a pellet of compound under study with a mass of ca. 1 g was placed in a platinum crucible and weighed to $\pm 10^{-5} \text{ g}$ with a Mettler AT201 balance. The crucible with the sample was adjusted to

the sample holder in the bomb head. The cotton thread fuse of empirical formula $\text{CH}_{1.887}\text{O}_{0.902}$ and $\Delta_c u^\circ = -16\,565.9 \pm 8.6 \text{ J}\cdot\text{g}^{-1}$ ¹⁶ was tied to the platinum ignition wire (Johnson Matthey; mass fraction: 0.9995; diameter 0.05 mm), which was then connected between the two discharge electrodes. A volume of 1.0 cm³ of distilled and deionized water from a Millipore system (conductivity, $<0.1 \mu\text{S}\cdot\text{cm}^{-1}$) was added to the bomb body by means of a volumetric pipet. The stainless steel bomb (Parr 1108) of 340 cm³ internal volume was assembled and purged twice by successively charging it with oxygen at a pressure of 1.01 MPa and venting the overpressure. After purging, the bomb was charged with oxygen at a pressure of 3.04 MPa and a few minutes were allowed for equilibration before closing the inlet valve. The bomb was placed in the calorimeter proper, inside the thermostatic bath. On average the calorimeter proper contained 3751.99 g of distilled water. The combustion of the sample was initiated by discharge of a 2990 μF capacitor from a potential of $\approx 40 \text{ V}$ through the platinum wire.

The completeness of the combustion was confirmed in each experiment by gravimetric analysis of the amount of carbon dioxide formed.^{36,37} On average, the ratio of the mass of CO_2 obtained in the analysis to that expected from the mass of sample weighed was 0.999 ± 0.001 .

The nitric acid formed in the calorimetric process from traces of atmospheric N_2 remaining inside the bomb after purging was determined by titration with aqueous sodium hydroxide (Merck titrisol, $0.01 \text{ mol}\cdot\text{dm}^{-3}$), using methyl red as the indicator.

Sublimation Calorimetry. The enthalpies of sublimation of the three hydroxybenzoic acid isomers were measured by using the electrically calibrated Calvet drop-sublimation micro-calorimeter and the operating procedure previously reported.³⁸

Each run involved the recording of three measuring curves corresponding to the pumping background, the electrical calibration, and the sublimation of the sample, respectively. The temperature of the calorimeter was set at 340.15 K in the case of 2-OHBA, and at 388.15 K for 3-OHBA and 4-OHBA. The reference and sample cells, both initially empty and under argon atmosphere, were simultaneously evacuated using a pumping system whose ultimate vacuum was $4 \times 10^{-3} \text{ Pa}$. The pumping background and calibration curves were recorded in sequence. Argon was admitted to the cells, and once a stable baseline was observed, a thin capillary containing 3–10 mg of sample, which had been weighed with a precision of 10^{-7} g in a Mettler UMT2 ultra-micro balance, was dropped into the sample cell. An endothermic peak due to the heating of the sample from room temperature to the temperature of the calorimeter was first observed. After the signal returned to the baseline, the evacuation of the cells was started and the measuring curve corresponding to the sublimation of the sample was acquired.

Theoretical Calculations. Theoretical results were based on density functional theory (DFT) and ab initio complete basis set extrapolation procedures. All calculations were performed with the Gaussian-98 package.³⁹ Full geometry optimizations and frequency calculations were carried out with two hybrid functionals: B3PW91, which is a combination of the Becke's three parameter functional (B3)⁴⁰ with the Perdew and Wang nonlocal correlation functional (PW91),⁴¹ and MPW1PW91, which combines the modified Perdew–Wang exchange (MPW1)⁴² with the PW91 correlation functional.⁴¹ Geometry optimizations and frequency calculations were carried out with the aug-cc-pVDZ basis set.^{43,44} The corresponding electronic energies at 0 K were converted to standard enthalpies at 298.15 K by using zero point energy and thermal energy corrections calculated at the same level of theory. MPW1PW91 single-point

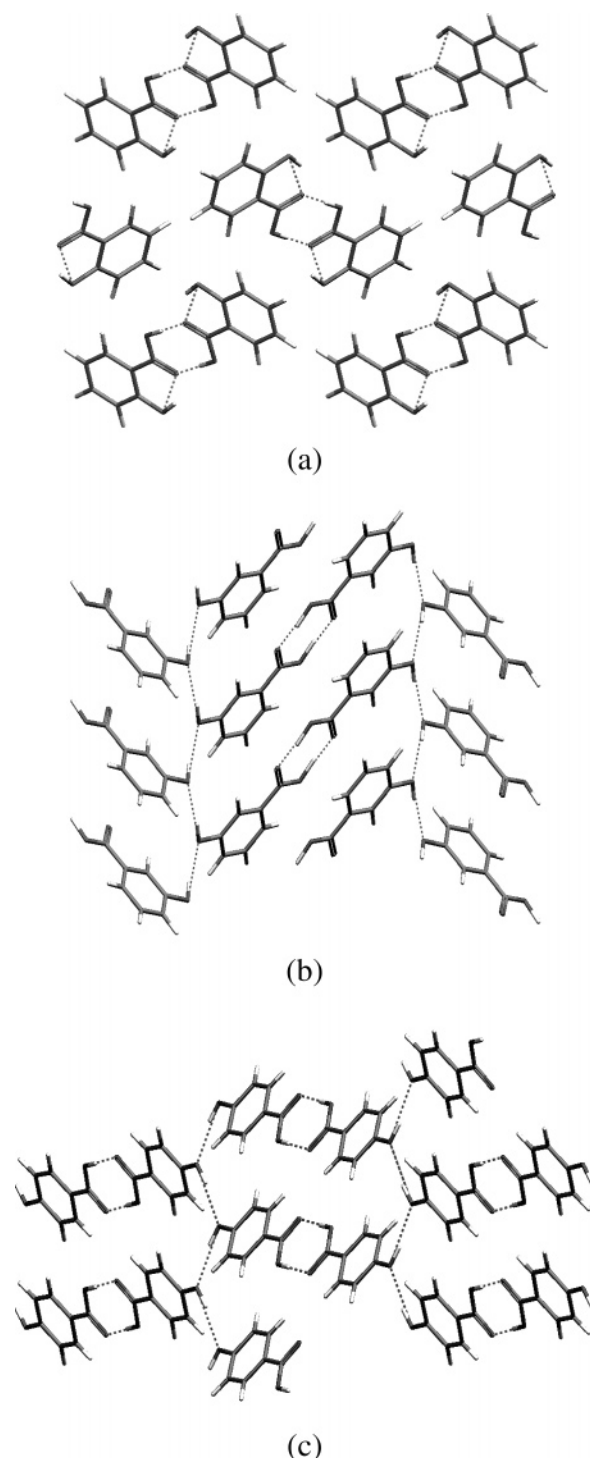


Figure 1. Crystal structure of (a) 2-hydroxybenzoic acid (projected on the ab plane), (b) 3-hydroxybenzoic acid (projected on the bc plane), and (c) 4-hydroxybenzoic acid (projected on the ab plane).

energies with the aug-cc-pVTZ basis set^{43,44} were also carried out. In this case, the conversion of the computed electronic energies at 0 K to standard enthalpies at 298.15 K was based on structural and vibration frequency data obtained using the MPW1PW91/aug-cc-pVDZ results. Heat capacities have been computed at different temperatures at the B3PW91/aug-cc-pVDZ level. The ab initio complete basis set extrapolation procedure CBS-QMPW1³² was also applied for estimating thermochemical properties. The CBS-QMPW1³² procedure is a modified CBS-QB3^{45,46} scheme in which geometries and frequencies are based on MPW1PW91/aug-cc-pVDZ calculations.

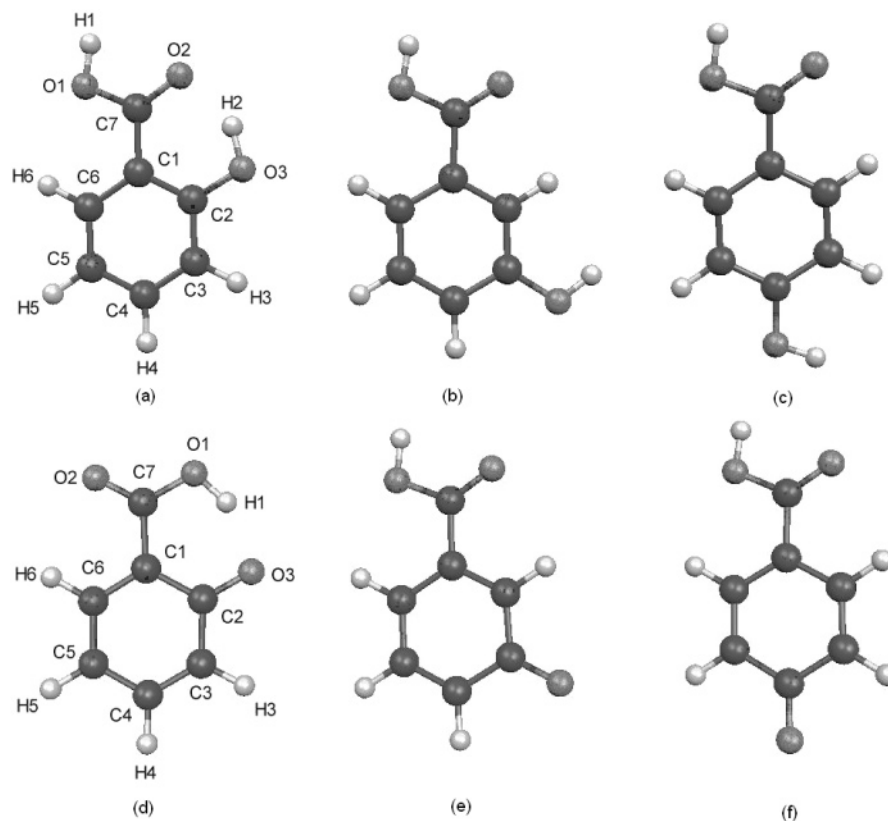


Figure 2. Calculated molecular structures of the most stable conformations of (a) 2-hydroxybenzoic acid, (b) 3-hydroxybenzoic acid, (c) 4-hydroxybenzoic acid, (d) 2-carboxyphenoxy radical, (e) 3-carboxyphenoxy radical, and (f) 4-carboxyphenoxy radical.

Results and Discussion

Structure. Drawings of the crystal structures of monoclinic 2-, 3-, and 4-OHBA, obtained from previously reported neutron diffraction (2-OHBA)^{47,48} and X-ray diffraction data (3- and 4-OHBA),^{29,30,48} by using the programs Conquest 1.5 and Mercury 1.1.2⁴⁹ are shown in Figure 1. In all cases pairs of hydroxybenzoic acid molecules form cyclic H-bonded dimers involving the carboxylic groups, a structural motif usually exhibited by carboxylic acids. These bonds with O–H–O angles of 179.0° (2-OHBA), 172.12° (3-OHBA), and 176.93° (4-OHBA) are almost linear, as is normally found for carboxylic acids. The HO---OC distances of 263.6 pm (2-OHBA),^{47–49} 261.7 pm (3-OHBA),^{29,48,49} and 263.4 pm (4-OHBA)^{30,48,49} are also in the range typically found for this type of bond (250–320 pm).¹⁰ The dimers of 3- and 4-OHBA are held together in chains by H-bonds between the phenolic groups. In 2-OHBA they are independent, because each phenolic group is involved in an intramolecular H-bond with the CO carboxylic group as the acceptor. As will be apparent below, these structural differences are clearly reflected by differences in enthalpies of sublimation, i.e., $\Delta_{\text{sub}}H_m^0(2\text{-OHBA}) < \Delta_{\text{sub}}H_m^0(3\text{-OHBA}) \approx \Delta_{\text{sub}}H_m^0(4\text{-OHBA})$. A full comparison of the experimental bond distances and angles found in the solid state with those for the most stable conformers predicted by the B3PW91/aug-cc-pVDZ and MPW1PW91/aug-cc-pVDZ calculations (see Figure 2) is included in the Supporting Information. Only the most significant details are given here (Table 1). The differences in bond distances noted for the C–C skeleton are in general smaller than 2 pm. As expected, larger deviations are observed for distances between atoms involved in H-bonds in the solid state but not in the gaseous state. Thus the experimental C7–O1 bond distance in 2-, 3-, and 4-OHBA and the C7–O2 bond distance in 3- and 4-OHBA are significantly shorter than the

computed ones (Table 1). The theoretical calculations accurately predict the bond distances between the heavy atoms involved in the intramolecular H-bond of 2-OHBA (C7–O2 and O2–O3), but they yield shorter O1–H1 and longer O3–H2 distances when compared with the corresponding neutron diffraction results. The last two observations are not unexpected because (i) the O1–H1 bond will be weaker (and therefore longer) in the solid state because H1 is involved in intermolecular bonding and (ii) the O3–H2 bond will be stronger in the solid state because O2 is involved in intermolecular H-bonding, therefore weakening the H2---O2 intramolecular bond. This is in keeping with the considerably smaller O2---H2 distance predicted by the B3PW91/aug-cc-pVDZ (170.3 pm) and MPW1PW91/aug-cc-pVDZ (170.4 pm) models when compared with the neutron diffraction data (176.6 pm). Note also that the results predicted for the O2–H2–O3 bond angle in 2-OHBA by the B3PW91/aug-cc-pVDZ (147.8°) and MPW1PW91/aug-cc-pVDZ (147.6°) models are in good agreement with the neutron diffraction result (145.4°).

The complete set of bond distances and angles predicted by B3PW91/aug-cc-pVDZ, and MPW1PW91/aug-cc-pVDZ calculations for the most stable conformers of the radicals 2-HOOC₆H₄O•, 3-HOOC₆H₄O•, and 4-HOOC₆H₄O• (Figure 2) are included in the Supporting Information. A selection of the most relevant data is listed in Table 2. The calculated structures of the radicals are very similar to those of the corresponding precursors except in the vicinity of the phenoxy radical site. Thus, for example, the C–C(O•) bond distances in the radicals are always ca. 5 pm longer than the C–C(OH) and the C–O• distances are shorter than the C–OH distances in the acids by 5–10 pm depending on the calculation method.

As shown in Figure 2, on cleavage of the O3–H2 bond in 2-OHBA to yield the corresponding 2-HOOC₆H₄O• radical,

TABLE 1: Calculated and Experimental Bond Distances (pm) and Bond Angles (deg) for 2-, 3-, and 4-OHBA

	2-OHBA			3-OHBA			4-OHBA		
	B3PW91/ aug-cc-pVDZ	MPW1PW91/ aug-cc-pVDZ	exp (solid) ^a	B3PW91/ aug-cc-pVDZ	MPW1PW91/ aug-cc-pVDZ	exp (solid) ^a	B3PW91/ aug-cc-pVDZ	MPW1PW91/ aug-cc-pVDZ	exp (solid) ^a
C7-O1	134.6	134.2	130.0	135.4	135.0	126.1 ± 0.2	135.7	135.3	126.6 ± 0.2
C7-O2	123.1	122.8	123.1	121.4	121.1	126.9 ± 0.3	121.5	121.2	126.6 ± 0.2
C2-O3	133.9	133.6	136.0						
C3-O3				136.4	136.1	138.9 ± 0.2			
C4-O3							135.9	135.6	137.7 ± 0.2
O1-H1	96.9	96.7	98.6	96.9	96.7	115.0 ± 4.0	96.9	96.7	83.1
O3-H2	98.8	98.5	95.4	96.4	96.2	84.2 ± 4.0	96.4	96.2	87.4
O2--H2	170.4	170.3	176.6						
O2--O3	259.3	258.9	260.8						
O1-C7-O2	120.7	120.7	121.0	121.9	121.9	123.6 ± 0.2	121.7	121.7	123.2 ± 0.2
O2-C7-C1	124.3	124.3	123.0	124.8	124.8	118.2 ± 0.2	125.1	125	118.2 ± 0.1
C7-C1-C2	118.5	118.5	119.7						
C1-C2-O3	122.5	122.5	122.8						
H1-O1-C7	106.3	106.4	112.4	105.9	106	115 ± 2	105.7	105.8	113.6
H2-O3-C3				109.4	109.5	105 ± 2			
H2-O3-C4							109.6	109.7	108.4
O2--H2-O3	147.8	147.6	145.4						

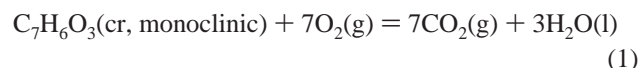
^a 2-OHBA, neutron diffraction, refs 47–49; 3-OHBA, X-ray diffraction, refs 29, 48, 49; 4-OHBA, X-ray diffraction, refs 30, 48, 49.

TABLE 2: Calculated Bond Distances (pm) and Bond Angles (deg) for the Carboxyphenoxy Radicals

	2-HOOCPhO [•]		3-HOOCPhO [•]		4-HOOCPhO [•]	
	B3PW91/ aug-cc-pVDZ	MPW1PW91/ aug-cc-pVDZ	B3PW91/ aug-cc-pVDZ	MPW1PW91/ aug-cc-pVDZ	B3PW91/ aug-cc-pVDZ	MPW1PW91/ aug-cc-pVDZ
C7-O1	133.2	132.8	135.3	134.9	135.2	134.9
C7-O2	121.1	120.9	121.0	120.8	121.3	121.0
C2-O3	126.0	125.7				
C3-O3			125.5	125.3		
C4-O3					125.1	124.9
O1-H1	99.2	98.9	96.9	96.7	96.9	96.7
O3--H1	168.3	168.4				
O1--O3	260.1	259.9				
O1-C7-O2	122.5	122.5	122.6	122.6	122.5	122.5
C7-C1-C2	122.5	122.3				
C1-C2-O3	121.7	121.6				
O2-C7-C1			124.7	124.6	124.3	124.3
O3-C3-C2			121.2	121.2		
H1-O1-C7	108.1	108.2	106.2	106.3	106.3	106.4
O1-C7-C1	116.2	116.3				
O1-H1--O3	152.2	152.0				
O3-C4-C3					121.5	121.4

the carboxylic acid group rotates and the H2---O2 intramolecular H-bond in the precursor is replaced by the H1---O3 in the radical. Despite the change of the nature of the H-bond in 2-OHBA and in the corresponding radical, the distance between the oxygen atoms involved in those bonds remains practically the same (Tables 1 and 2), i.e., O2---O3 = 259.3 pm (B3PW91/aug-cc-pVDZ); 258.9 pm (MPW1PW91/aug-cc-pVDZ) and O1---O3 = 260.1 pm (B3PW91/aug-cc-pVDZ); 259.9 pm (MPW1PW91/aug-cc-pVDZ).

Energetics. The 2001 IUPAC recommended standard atomic masses were used in the calculation of all molar quantities.⁵⁰ The standard internal energies and enthalpies of combustion of monoclinic 3- and 4-hydroxybenzoic acids at 298.15 K, obtained in the combustion calorimetry experiments were $\Delta_c u^0(3\text{-OHBA}) = -21\,851.75 \pm 1.68 \text{ J}\cdot\text{g}^{-1}$, $\Delta_c H_m^0(3\text{-OHBA}) = -3018.2 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_c u^0(4\text{-OHBA}) = -21\,827.58 \pm 1.37 \text{ J}\cdot\text{g}^{-1}$, and $\Delta_c H_m^0(4\text{-OHBA}) = -3014.8 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. The uncertainties quoted for $\Delta_c u^0$ represent the standard deviation of the mean of six individual results (see Supporting Information) and those of $\Delta_c H_m^0$ correspond to twice the overall standard deviation of the mean, including the contributions from the calibration with benzoic acid.⁵¹ The above results refer to the reaction



and lead to the corresponding standard molar enthalpies of formation listed in Table 3, by using $\Delta_f H_m^0(\text{CO}_2, \text{g}) = -393.51 \pm 0.13 \text{ kJ}\cdot\text{mol}^{-1}$ ⁵² and $\Delta_f H_m^0(\text{H}_2\text{O}, \text{l}) = -285.830 \pm 0.040 \text{ kJ}\cdot\text{mol}^{-1}$.⁵²

The enthalpies of sublimation of 2-, 3-, and 4-OHBA obtained by Calvet drop-sublimation microcalorimetry were $\Delta_{\text{sub}} H_m^0(2\text{-OHBA}) = 93.28 \pm 0.35 \text{ kJ}\cdot\text{mol}^{-1}$ at 340.15 K, $\Delta_{\text{sub}} H_m^0(3\text{-OHBA}) = 116.10 \pm 1.10 \text{ kJ}\cdot\text{mol}^{-1}$ at 388.15 K, and $\Delta_{\text{sub}} H_m^0(4\text{-OHBA}) = 114.56 \pm 0.52 \text{ kJ}\cdot\text{mol}^{-1}$ at 388.15 K. The uncertainties quoted represent twice the standard deviation of the mean of five results for 2- and 4-OHBA, and eight results in the case of 3-OHBA. The values of the enthalpies of sublimation at the temperature of the experiments, $\Delta_{\text{sub}} H_m^0(T)$, indicated above were corrected to 298.15 K (Table 3) by using

$$\Delta_{\text{sub}} H_m^0(298.15 \text{ K}) = \Delta_{\text{sub}} H_m^0(T) + \int_T^{298.15\text{K}} [C_{p,m}^0(\text{g}) - C_{p,m}^0(\text{cr})] dT \quad (2)$$

where $C_{p,m}^0(\text{cr})$ and $C_{p,m}^0(\text{g})$ are the molar heat capacities of the

TABLE 3: Enthalpies of Formation and Sublimation ($\text{kJ}\cdot\text{mol}^{-1}$) of 2-, 3-, and 4-Hydroxybenzoic Acids at 298.15 K

compound	$-\Delta_f H_m^0(\text{cr})$	$\Delta_{\text{sub}} H_m^0$	$-\Delta_f H_m^0(\text{g})$
2-OHBA	591.7 ± 1.3^a	94.4 ± 0.4^b	497.3 ± 1.4^b
	586.1 ± 1.9^c		
	587.1^d		
	587.8 ± 1.5^e		
	588.9 ± 1.5^f		
	589.1 ± 3.0^g		
	589.4 ± 1.1^h	96.2 ± 0.6^b	493.2 ± 1.3
	589.9 ± 1.0^i		
	592.1 ± 1.6^j	96.1 ± 1.0^l	496.0 ± 1.9
	594.5 ± 2.9^k		
3-OHBA	593.9 ± 2.0^b	118.3 ± 1.1^b	475.6 ± 2.3^b
	590.5 ± 1.0^b		
	594.2 ± 1.4^j	125.0 ± 1.5^j	469.2 ± 2.1
	597.2 ± 1.4^b	117.0 ± 0.5^b	480.2 ± 1.5^b
	594.5 ± 1.0^h		
	606.7 ± 2.3^j	114.0 ± 1.4^j	492.7 ± 2.7
4-OHBA		85.9 ± 0.9^l	
		98.1 ± 0.4^m	
		99.3 ± 4.2^n	
		95.6 ± 0.8^o	
		93.8 ± 1.7^o	
		120.1 ± 0.8^m	

^a Reference 16, monoclinic phase. ^b This work, monoclinic phase. ^c Reference 17. ^d Reference 18. ^e Reference 19. ^f Reference 20. ^g Reference 21. ^h Reference 3. ⁱ References 22 and 23. ^j Reference 4. ^k Reference 24. ^l Reference 25. ^m Reference 2. ⁿ Reference 26. ^o Reference 27.

TABLE 4: Values of the a and b Parameters Used to Calculate $C_{p,m}^0$ in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ from Eq 3

Compound		$a/\text{J}\cdot\text{K}^{-2}\cdot\text{mol}^{-1}$	$b/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	Temperature range/K
2-OHBA	(cr)	0.5097	8.9585	298–340
	(g)	0.3955	18.4021	298–400
3-OHBA	(cr)	0.5070	10.4383	231–288
	(g)	0.3866	26.8130	298–400
4-OHBA	(cr)	0.5188	8.2349	229–284
	(g)	0.3869	26.4640	298–400

compounds in the crystalline and gaseous states, respectively. The temperature dependences of the heat capacities in eq 2 were obtained by least-squares fitting of the equation

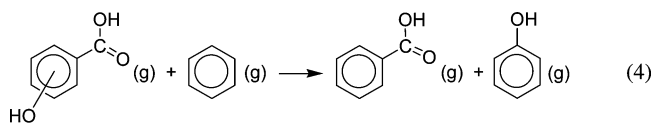
$$C_{p,m}^0 = aT + b \quad (3)$$

to data reported in the literature for the crystalline acids,^{53,54} or computed in this work by DFT (B3PW91/aug-cc-pVDZ) in the case of the gaseous species. The obtained values for the a and b parameters of eq 3 that give $C_{p,m}^0$ in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ are shown in Table 4.

The standard molar enthalpies of formation and sublimation of monoclinic 2-, 3-, and 4-hydroxybenzoic acids, at 298.15 K are compared in Table 3 with data previously reported by us and other authors, who used samples of unspecified phase purity.^{2–4,16–27} Also indicated in Table 3 are the corresponding enthalpies of formation in the gaseous state. The most significant differences between the present $\Delta_f H_m^0(\text{g})$ results and the literature data are found for 3-OHBA ($6.4 \text{ kJ}\cdot\text{mol}^{-1}$) and 4-OHBA ($12.5 \text{ kJ}\cdot\text{mol}^{-1}$).

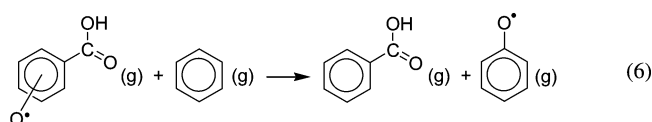
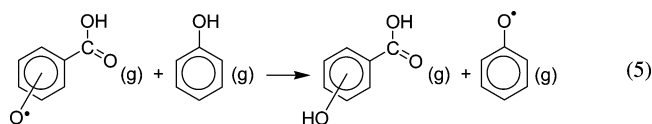
The experimental enthalpies of formation of gaseous 2-, 3-, and 4-OHBA in conjunction with $\Delta_f H_m^0(\text{C}_6\text{H}_6, \text{g}) = (82.6 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1}$,⁵⁵ $\Delta_f H_m^0(\text{C}_6\text{H}_5\text{OH}, \text{g}) = -(96.4 \pm 0.9) \text{ kJ}\cdot\text{mol}^{-1}$,⁵⁵ and $\Delta_f H_m^0(\text{C}_6\text{H}_5\text{COOH}, \text{g}) = -(294.0 \pm 2.2)$

$\text{kJ}\cdot\text{mol}^{-1}$,⁵⁵ allow the calculation of the enthalpy of the isodesmic and isogyric reaction 4. As shown in Table 5,



the obtained results are in good agreement with the predictions of the B3PW91/aug-cc-pVDZ, MPW1PW91/aug-cc-pVDZ, MPW1PW91/aug-cc-pVTZ//MPW1PW91/aug-cc-pVDZ, and CBS-QMPW1 methods. For each OHBA isomer, the two DFT approaches (B3PW91 and MPW1PW91) lead to quite similar $\Delta_f H_m^0(4)$ values. In addition, comparison of the MPW1PW91 calculations with the aug-cc-pVDZ and aug-cc-pVTZ basis sets suggests that the calculations are not significantly dependent on the basis set. The CBS-QMPW1 procedure gives the best agreement with the experimental data. This supports the reliability of the CBS-QMPW1 results and indicates a very good thermodynamic consistency between the theoretical $\Delta_f H_m^0(4)$ values and the corresponding experimental results derived from standard enthalpy of formation data. The CBS-QMPW1 method has been recently applied to investigate the energetics of intramolecular H-bonding in disubstituted benzenes and its accuracy was shown to be similar to that of the standard CBS-QB3 method.³²

The standard enthalpies of formation of the carboxyphenoxyl radicals 2-HOCC₆H₄O[•], 3-HOCC₆H₄O[•], and 4-HOCC₆H₄O[•] in the gaseous state, at 298.15 K, were estimated according to the following procedure. First, the enthalpies of reactions 5 and 6 were computed by using the different theoretical approaches (B3PW91/aug-cc-pVDZ, MPW1PW91/aug-cc-pVDZ, MPW1PW91/aug-cc-pVTZ, and CBS-QMPW1). The theoretical results for $\Delta_f H_m^0(5)$ or $\Delta_f H_m^0(6)$ were then combined with experimental enthalpy of formation data for the different species involved in reactions 5 and 6 to estimate $\Delta_f H_m^0(x\text{-HOCC}_6\text{H}_4\text{O}^\bullet, \text{g})$ ($x = 2, 3$, or 4) from eqs 7 or 8. The



$$\Delta_f H_m^0(x\text{-HOCC}_6\text{H}_4\text{O}^\bullet, \text{g}) = -\Delta_f H_m^0(5) + \Delta_f H_m^0(x\text{-OHBA}, \text{g}) + \Delta_f H_m^0(\text{C}_6\text{H}_5\text{O}^\bullet, \text{g}) - \Delta_f H_m^0(\text{C}_6\text{H}_5\text{OH}, \text{g}) \quad (7)$$

$$\Delta_f H_m^0(x\text{-HOCC}_6\text{H}_4\text{O}^\bullet, \text{g}) = -\Delta_f H_m^0(6) + \Delta_f H_m^0(\text{C}_6\text{H}_5\text{COOH}, \text{g}) + \Delta_f H_m^0(\text{C}_6\text{H}_5\text{O}^\bullet, \text{g}) - \Delta_f H_m^0(\text{C}_6\text{H}_6, \text{g}) \quad (8)$$

obtained values are shown in Table 6. They are based on the enthalpies of formation of gaseous 2-, 3-, and 4-OHBA reported in this work (Table 3), on the enthalpies of formation of benzene, phenol, and benzoic acid indicated above, and on the enthalpy of formation of the phenoxyl radical, $\Delta_f H_m^0(\text{C}_6\text{H}_5\text{O}^\bullet, \text{g}) = 56.9 \pm 2.4 \text{ kJ}\cdot\text{mol}^{-1}$.⁵⁶ The overall uncertainties assigned to the $\Delta_f H_m^0(x\text{-HOCC}_6\text{H}_4\text{O}^\bullet, \text{g})$ values refer to the contribu-

TABLE 5: Theoretical and Experimental Enthalpies (kJ·mol⁻¹) of Reactions 4–6 at 298.15 K

	B3PW91/ aug-cc-pVDZ	MPW1PW91/ aug-cc-pVDZ	MPW1PW91/ aug-cc-pVTZ	CBS-QMPW1	exp
Reaction 4					
2-OHBA	28.5	28.6	28.4	25.1	24.3 ± 2.8
3-OHBA	0.6	0.3	0.5	3.6	2.6 ± 3.4
4-OHBA	5.6	5.4	5.6	4.9	7.2 ± 2.9
Reaction 5					
2-HOOCPhO•	-25.3	-26.1	-25.3	-21.9	
3-HOOCPhO•	-9.4	-9.2	-9.2	-12.8	
4-HOOCPhO•	-10.7	-10.8	-10.8	-7.6	
Reaction 6					
2-HOOCPhO•	3.2	2.6	3.1	3.2	
3-HOOCPhO•	-8.8	-8.9	-8.7	-9.3	
4-HOOCPhO•	-5.1	-5.4	-5.2	-2.7	

TABLE 6: Enthalpy of Formation (kJ·mol⁻¹) of the Carboxyphenoxy Radicals at 298.15 K

method/reaction	reaction	-Δ _f H _m ^o (g)		
		2-HOOCPhO•	3-HOOCPhO•	4-HOOCPhO•
B3PW91/aug-cc-pVDZ	5	318.7 ± 2.9	312.9 ± 3.4	316.2 ± 3.0
	6	322.9 ± 3.3	310.9 ± 3.3	314.3 ± 3.3
MPW1PW91/aug-cc-pVDZ	5	317.9 ± 2.9	313.1 ± 3.4	316.1 ± 3.0
	6	322.8 ± 3.3	310.8 ± 3.3	314.3 ± 3.3
MPW1PW91/aug-cc-pVTZ	5	318.7 ± 2.9	313.1 ± 3.4	316.1 ± 3.0
	6	322.8 ± 3.3	311.0 ± 3.3	314.5 ± 3.3
CBS-QMPW1	5	322.1 ± 2.9	309.5 ± 3.4	319.3 ± 3.0
	6	322.9 ± 3.3	310.4 ± 3.3	317.0 ± 3.3

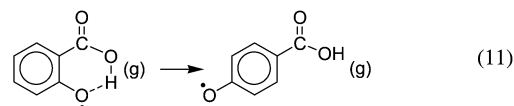
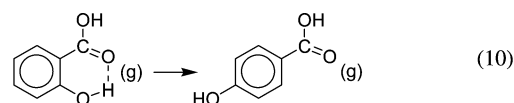
tions of the uncertainties of the experimental data used in the calculation. The enthalpies of formation of the radicals predicted from reactions 5 or 6 by all DFT models are in excellent agreement. They are also very close to the CBS-QMPW1 results. The fact that the different theoretical methods lead to very similar values for Δ_fH_m^o(x-HOOC₆H₄O•, g) indicates a good thermodynamic consistency between the theoretical reaction enthalpies and the experimental standard enthalpies of formation used as auxiliary data. The mean Δ_fH_m^o(x-HOOC₆H₄O•, g) values obtained from reactions 5 and 6 by the CBS-QMPW1 results were selected as the most accurate estimates of the enthalpy of formation of the carboxyphenoxy radicals: Δ_fH_m^o(2-HOOC₆H₄O•, g) = -322.5 ± 3.0 kJ·mol⁻¹, Δ_fH_m^o(3-HOOC₆H₄O•, g) = -310.0 ± 3.0 kJ·mol⁻¹, and Δ_fH_m^o(4-HOOC₆H₄O•, g) = -318.2 ± 3.0 kJ·mol⁻¹ (the uncertainties are conservative estimates). This choice is supported by the excellent agreement between the results of the CBS-QMPW1 calculations for reaction 4 and the corresponding experimental data.

Our selections for Δ_fH_m^o(x-HOOC₆H₄O•, g), together with the enthalpies of formation of 2-, 3-, and 4-OHBA obtained in this work (Table 3) and Δ_fH_m^o(H, g) = 217.998 ± 0.006 kJ·mol⁻¹,⁵² yield the following bond dissociation enthalpies at 298.15 K: DH^o(2-HOOC₆H₄O-H) = (392.8 ± 3.3) kJ·mol⁻¹, DH^o(3-HOOC₆H₄O-H) = (383.6 ± 3.8) kJ·mol⁻¹, and DH^o(4-HOOC₆H₄O-H) = (380.0 ± 3.4) kJ·mol⁻¹. These values are larger than DH^o(PhO-H) = (371.3 ± 2.3) kJ·mol⁻¹⁵⁶ by 21.5 ± 4.0, 12.3 ± 4.4, and 8.7 ± 4.1 kJ·mol⁻¹, respectively, in keeping with the general observation that electron withdrawing substituents strengthen the O-H bond in monosubstituted phenols, relative to phenol.⁵⁶ It is also interesting to note that, based on the Hammett parameters σ⁺(3-COOH) = 0.32 and σ⁺(4-COOH) = 0.42,⁵⁷ the previously reported correlation (X = meta or para substituent; DH^o in kJ·mol⁻¹)⁵⁶

$$DH^o(XC_6H_4O-H) - DH^o(PhO-H) = 28.13\sigma^+ - 2.08 \quad (9)$$

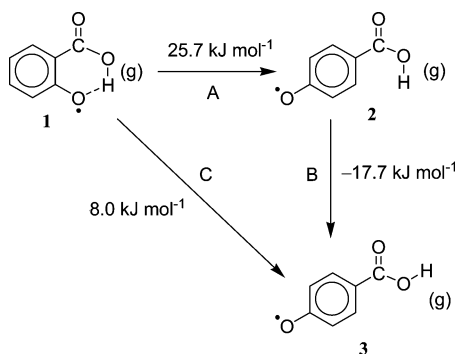
leads to DH^o(3-HOOC₆H₄O-H) = 378 kJ·mol⁻¹ and DH^o(4-HOOC₆H₄O-H) = 381 kJ·mol⁻¹, which agree with the values reported in this work within their experimental errors.

Finally our results allow us to analyze the energetics of the intramolecular H-bonds in 2-OHBA and in the 2-HOOC₆H₄O• radical based on the recently proposed ortho-para method.³² As seen in Figure 2, the nature of these bonds is different: whereas the donor in 2-OHBA is the -OH phenolic group and the acceptor is the carboxylic -CO group, in 2-HOOC₆H₄O• the donor is the carboxylic -OH group and the acceptor the phenoxy -O• group. The computation of an intramolecular H-bond enthalpy requires the selection of a reference structure. In the ortho-para method 4-OHBA is used as reference system for 2-OHBA, because it is generally agreed that electronic effects of the ortho- and para-OH substituent on the molecular energetics are comparable.^{5,57-59} A similar approach is used for the 2-carboxyphenoxy radical. The intramolecular H-bond enthalpies in 2-OHBA and 2-HOOC₆H₄O• are therefore given by the enthalpies of reactions 10 and 11 calculated as DH^o(-CO---HO-) = 20.2 kJ·mol⁻¹ and DH^o(-OH---O•-) = 5.9 kJ·mol⁻¹. The theoretical result for the H-bond in 2-OHBA agrees with the value obtained from the experimental enthalpies of formation, 17.1 ± 2.1 kJ·mol⁻¹ (reaction 10). According to the classification reported by Jeffrey,¹⁰ the former corresponds to a moderately strong H-bond and the latter to a weak H-bond.



The H-bond in 2-OHBA is 11 kJ·mol⁻¹ stronger than in catechol (9.6 kJ·mol⁻¹).³² This is consistent with the respective H---O distances, 170 and 214 pm, and also with the O-H---O

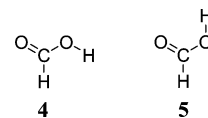
SCHEME 1



angles, 149° in 2-OHBA and 114° in catechol (i.e., the H-bond in 2-OHBA is closer to linearity than in catechol). A similar trend has been noted by Foti et al., involving 1,8-naphthalenediol, where the H-bond is part of a six-membered ring (as in 2-OHBA), and catechol.⁶⁰

On the other hand, the present results seem to indicate that the H-bond enthalpy in 2-OHBA is about 12 kJ·mol⁻¹ stronger than in its radical. This contrasts to what has been reported for catechol, where the H-bond (calculated at the same theory level and also using the ortho-para method, viz. 9.6 kJ·mol⁻¹) is some 15 kJ·mol⁻¹ weaker than in the radical (25.1 kJ·mol⁻¹).³² Furthermore, the computed H---O distances in 2-OHBA and in 2-carboxyphenoxyl radical (170 vs 168 pm; see Tables 1 and 2) suggest that the H-bond enthalpy in the parent should be somewhat weaker than in the radical. In fact, it is well-known that bond “strengths” correlate with bond lengths, i.e., for bonds of similar nature the shorter the bond the higher its bond enthalpy.⁶¹ However, this correlation may not be observed if the bond “strengths” are identified with bond dissociation enthalpies, because these parameters include the relaxation energies of the fragments formed upon cleavage of the bond.^{61,62} Therefore, the apparent contradiction noted above can be understood along these lines with the help of Scheme 1, where reaction 11 is given as the combination of two steps, A and B. Structures 1 and 3 represent the most stable conformers of reactant and product of reaction 11, whereas in structure 2 the carboxyl group remains in the same conformation as in 1. The enthalpy of step A will therefore measure the “intrinsic” H-bond, according to the ortho-para method. Step B, involving the 180° rotation of the C-OH bond, is simply the relaxation of 2 to its more stable conformer 3. In other words, the H-bond dissociation enthalpy in the 2-carboxyphenoxyl radical (the enthalpy of step C) is necessarily smaller than the enthalpy of step A because the fragment 2 relaxes to its most stable conformer.

The computation of the enthalpies of steps A, B, and C at the MPW1PW91/aug-cc-pVDZ level, yields +25.7, -17.7, and +8.0 kJ·mol⁻¹, respectively (the last value is quite similar to the one obtained for the enthalpy of reaction 11 at the CBS-QMPW1 level, 5.9 kJ·mol⁻¹). Therefore, the intrinsic H-bond enthalpy (given by the enthalpy of step A) is quite strong and is in keeping with the expected bond length-bond strength relationship. However, the relaxation step B is rather exothermic, so that the overall process is only 8 kJ·mol⁻¹ endothermic. The large stabilization of structure 3 relative to 2 is probably due to the carbonyl-hydroxyl interaction in the carboxyl group. This conclusion is supported by the results of MPW1PW91/aug-cc-pVDZ calculations on two conformers of a simpler molecule, formic acid, whose structures 4 and 5 differ by ca. 14 kJ·mol⁻¹, a value that is close to the one computed for step B.



Acknowledgment. This work was supported by Fundação para a Ciência e a Tecnologia (Projects POCTI/199/QUI/35406 and POCTI/43315/QUI/2001). The use of the supercomputing facilities in Linköping (NSC), Sweden, is acknowledged by R.C.G. Ph.D. grants from Fundação para a Ciência e a Tecnologia are also gratefully acknowledged by R.C.G. and S.S.P.

Supporting Information Available: Tables with the indexing of the X-ray powder diffraction lines for 3- and 4-hydroxybenzoic acids. Table with a comparison between calculated and experimental bond distances and angles for 2-, 3-, and 4-OHBA. Table with the computed bond distances and angles for the corresponding carboxyphenoxyl radicals. Tables with the results of all individual combustion experiments carried out on 3- and 4-hydroxybenzoic acids. Table with the total energies from the calculations, at 298.15 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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