J. Phys. Chem. A **2008,** *112,* 10029–10039 **10029**

Energetics of the O−H Bond and of Intramolecular Hydrogen Bonding in $HOC_6H_4C(O)Y$ (Y = H, CH_3, $CH_2CH{=}CH_2$, $C{\equiv}CH$, CH_2F, NH_2, $NHCH_3$, NO_2, OH, OCH_3, OCN, CN, F, Cl, SH, and SCH_3) Compounds

Carlos E. S. Bernardes and Manuel E. Minas da Piedade*

Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1649-016 Lisboa, Portugal

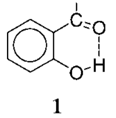
Received: May 20, 2008; Revised Manuscript Received: June 25, 2008

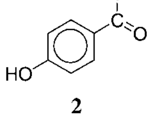
The energetics of the phenolic O−H bond in a series of 2- and 4-$HOC_6H_4C(O)Y$ (Y = H, CH_3, $CH_2CH{=}CH_2$, $C{\equiv}CH$, CH_2F, NH_2, $NHCH_3$, NO_2, OH, OCH_3, OCN, CN, F, Cl, SH, and SCH_3) compounds and of the intramolecular O···H hydrogen bond in 2-$HOC_6H_4C(O)Y$, was investigated by using a combination of experimental and theoretical methods. The standard molar enthalpies of formation of 2-hydroxybenzaldehyde (2HBA), 4-hydroxybenzaldehyde (4HBA), 2′-hydroxyacetophenone (2HAP), 2-hydroxybenzamide (2HBM), and 4-hydroxybenzamide (4HBM), at 298.15 K, were determined by micro- or macrocombustion calorimetry. The corresponding enthalpies of vaporization or sublimation were also measured by Calvet drop-calorimetry and Knudsen effusion measurements. The combination of the obtained experimental data led to $\Delta_f H_m^o$(2HBA, g) = −238.3 ± 2.5 $kJ \cdot mol^{-1}$, $\Delta_f H_m^o$(4HBA, g) = −220.3 ± 2.0 $kJ \cdot mol^{-1}$, $\Delta_f H_m^o$(2HAP, g) = −291.8 ± 2.1 $kJ \cdot mol^{-1}$, $\Delta_f H_m^o$(2HBM, g) = −304.8 ± 1.5 $kJ \cdot mol^{-1}$, and $\Delta_f H_m^o$ (4HBM, g) = −278.4 ± 2.4 $kJ \cdot mol^{-1}$. These values, were used to assess the predictions of the B3LYP/6-31G(d,p), B3LYP/6-311+G(d,p), B3LYP/aug-cc-pVDZ, B3P86/6-31G(d,p), B3P86/6-311+G(d,p), B3P86/aug-cc-pVDZ, and CBS-QB3 methods, for the enthalpies of a series of isodesmic gas phase reactions. In general, the CBS-QB3 method was able to reproduce the experimental enthalpies of reaction within their uncertainties. The B3LYP/6-311+G(d,p) method, with a slightly poorer accuracy than the CBS-QB3 approach, achieved the best performance of the tested DFT models. It was further used to analyze the trends of the intramolecular O···H hydrogen bond in 2-$HOC_6H_4C(O)Y$ evaluated by the ortho−para method and to compare the energetics of the phenolic O−H bond in 2- and 4-$HOC_6H_4C(O)Y$ compounds. It was concluded that the O−H bond "strength" is systematically larger for 2-hydroxybenzoyl than for the corresponding 4-hydroxybenzoyl isomers mainly due to the presence of the intramolecular O···H hydrogen bond in the 2-isomers. The observed differences are, however, significantly dependent on the nature of the substituent Y, in particular, when an intramolecular H-bond can be present in the radical obtained upon cleavage of the O−H bond.

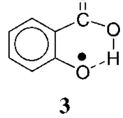
Introduction

The energetics of the O−H bond in aromatic compounds has been at the heart of many interesting chemical processes such as the depolymerization of coal[1,2] and the antioxidant activity of phenol derivatives.[3,4] This has fostered a variety of studies on the O−H bond dissociation enthalpy, $DH°$(O−H), trends with particular emphasis on the effect of substituents directly bonded to the ring system.[3] Much less well investigated is, however, the dependence of $DH°$(O−H) on the nature of substituents not directly attached to the aromatic ring. An interesting model to explore this effect is provided by 2- and 4-hydroxybenzoyl compounds.

There is ample evidence that the 2-hydroxybenzoyl isomers **1** exhibit an intramolecular hydrogen bond (H-bond) of moderate "strength" with the phenolic OH group functioning as the proton donor, and the CO group of the adjacent substituent, acting as the acceptor.[5,6] The formation of this O···H bond should confer an increased thermodynamic stability to the molecule, thus contributing to an increase in the phenolic O−H bond dissociation enthalpy relative to that in the 4-hydroxybenzoyl analogue **2**. It is also known that the corresponding $DH°$(O···H) can be influenced by the nature of the Y substituent[7−9] and this should also affect the corresponding O−H bond dissociation enthalpy. However, when considering $DH°$(O−H) trends, one should not exclusively focus on the initial state of the homolitic O−H bond scission (the precursor molecule). The nature of the substituent Y may also have an important effect on the stability of the radical resulting from breaking the O−H bond and on possible reorganization effects associated with its formation, which can both influence the corresponding $DH°$(O−H) value. In the case of 2-hydroxybenzoic acid, for example, it has been shown that $DH°$(O−H) considerably depends on the stabilization of the radical **3** formed upon breaking of the O−H bond, by an intramolecular $O^{\bullet}$···H bond of different nature from that existing in the precursor molecule.[10]


1


2


3

We have recently used a combination of experimental and computational chemistry methods to investigate the systematics of bond dissociation enthalpies in different types of organic molecules through isodesmic reaction schemes.[10−13] This strat-

---

* Corresponding author. E-mail: memp@fc.ul.pt.

10.1021/jp804455u CCC: $40.75

egy is applied in the present work to study the energetics of hydroxybenzoyl compounds, $HOC_6H_4C(O)Y$ (Y = H, CH_3, $CH_2CH{=}CH_2$, $C{\equiv}CH$, CH_2F, NH_2, $NHCH_3$, NO_2, OH, OCH_3, OCN, CN, F, Cl, SH, and SCH_3) with particular emphasis on the influence of the substituent Y on the O−H bond dissociation enthalpy.

Materials and Methods

Elemental analyses (C, H, N) were made on a Fisons Instruments EA1108. The refractive indexes of the liquid samples for the sodium D line (589 nm) were measured with a CETI Abbe refractometer. ^{1}H NMR spectra were obtained in $CDCl_3$ or DMSO-d_6, at ambient temperature, on a Bruker Ultrashield 400 MHz spectrometer. Mass spectra at 70 eV electron energy were recorded on a Fisons Instruments Trio 1000 apparatus. GC−MS experiments were performed on an Agilent 6890 gas chromatograph coupled to an Agilent 5973 *N* mass detector. A TRB-5MS capillary column from Teknokroma (5% diphenyl/95% dimethylpolysiloxane; 30 m × 0.25 mm I.D., 0.25 μm d_f) was used. The carrier gas was helium maintained at a constant pressure of 1.19 bar. A vaporization injector operating in the split mode (1:100), at 523 K, was employed, and the oven temperature was programmed as follows: 323 K (1 min), ramp at 10 K·min^{-1}, 523 K (10 min). The transfer line, ion source and quadrupole analyzer were maintained at 553, 503, and 423 K, respectively, and a solvent delay of 5 min was selected. In the full-scan mode, electron ionization mass spectra in the range 35−550 Da were recorded at 70 eV electron energy and with an ionization current of 34.6 μA. Data recording and instrument control were performed by the MSD ChemStation software from Agilent (G1701CA; version C.00.00). The identity of the analyzed compound was assigned by comparison of the mass-spectrometric results with the data in Wiley's reference spectral databank (G1035B, Rev D.02.00) and its purity was calculated from the normalized peak areas, without using correction factors to establish abundances. The X-ray powder diffractograms were recorded on a Philips PW1730 diffractometer operating in the $\theta-2\theta$ mode, with automatic data acquisition (APD Philips v.35B). The apparatus had a vertical goniometer (PW1820), a proportional xenon detector (PW1711), and a graphite monocromator (PW1752). A Cu Kα radiation source was used. The tube amperage was 30 mA and the tube voltage 40 kV. The diffractograms were recorded in the range $5° \leq 2\,\theta \leq 35°$, in the continuous mode, with a step size of 0.015°(2 θ), and an acquisition time of 1.5 s/step. The samples were mounted on an aluminum sample holder. The indexation of the powder patterns was performed using the program Checkcell.[14] Differential scanning calorimetry (DSC) experiments were carried out on Setaram DSC 111 or TA 2920 MTDSC instruments. In the first case the purging gas was nitrogen at a flow rate of 10 cm^3·min^{-1} and in the second case helium at a flow rate of 60 cm^3·min^{-1} was used. The compounds were sealed under air in aluminum crucibles. The temperature and heat flux scales of the calorimeters were calibrated by determining the temperature and enthalpy of fusion of indium (Perkin-Elmer, 99.999%).

Materials. 2-Hydroxybenzaldehyde. 2HBA (Aldrich, 99%) was purified by a triple fractional distillation at 310 K and 150 Pa. The obtained sample was stored in a Schlenk tube under N_2 atmosphere prior to use. Refractive index: n_D^{20} = 1.5740 (lit: n_D^{20} = 1.574)[15,16] ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.03 (s, O**H**, 1H), 9.86 (s, C**H**, 1H), 7.50 (m, C**H**, 2H), 7.00 (m, CH, 2H). Mass spectrum: *m/z* (relative intensity) 122 (61), 121 (100), 104 (12), 94 (3), 93 (15), 76 (18), 74 (5), 66 (6), 65 (30), 63 (8), 62 (6), 61 (6), 55 (3), 53 (7), 51 (4), 50 (13), 47 (4), 41 (4), 39 (53), 37 (12). The MS results are in agreement with those reported in a reference database.[17] The onset (T_{on}) and maximum (T_{max}) temperatures of the fusion peak, obtained by DSC at a scan rate β = 3 K·min^{-1}, were T_{on} = 274.58 ± 0.04 K and T_{max} = 278.68 ± 0.14 K, respectively, and the corresponding enthalpy of fusion, $\Delta_{fus}H_m^o$ = 13.3 ± 0.4 kJ·mol^{-1}. The uncertainties quoted for T_{on} and T_{max} are mean deviations and that for $\Delta_{fus}H_m^o$ corresponds to twice the mean deviation of three determinations. The samples had masses *m* in the range 32−47 mg. The indicated fusion temperatures are significantly higher than the recommended value T_{fus} = 266 K.[15]

4-Hydroxybenzaldehyde. 4HBA (Acrös, 99%) was purified by sublimation at 368 K and 1.3 Pa. The obtained sample was kept in a Schlenk tube under N_2 atmosphere prior to use. Elemental analysis for $C_7H_6O_2$: expected C 68.85%, H 4.95%; found C 68.69%, H 5.19% (average of two determinations). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (s, C**H**, 1H), 7.75 (d, C**H**, 2H), 6.91 (d, C**H**, 2H), 6.13 (s, O**H**, 1H). The powder pattern was indexed as monoclinic, space group $P2_1/c$, with a = 6.481(1) Å, b = 13.833(4) Å, c = 7.053(2) Å, β = 108.06(2)°. These values are in good agreement with the previously reported a = 6.453(5) Å, b = 13.810(8) Å, c = 7.044(6) Å, and β = 107.94(9)°.[18] DSC (fusion, β = 1 K·min^{-1}, m = 3−20 mg): T_{on} = 389.6 ± 0.1 K, T_{max} = 390.8 ± 0.2 K, and $\Delta_{fus}H_m^o$ = 20.3 ± 0.2 kJ·mol^{-1}. The indicated fusion temperatures are in good agreement with the published value T_{fus} = 390.15 K.[15]

2′-Hydroxyacetophenone. 2HAP (Aldrich, 99%) was purified by a triple fractional distillation at 310 K and 150 Pa. The obtained sample was stored in a Schlenk tube under N_2 atmosphere prior to use. Refractive index: n_D^{24} = 1.5577 (lit.: n_D^{24} = 1.558;[16] n_D^{20} = 1.5584[15]). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.28 (s, O**H**, 1H), 7.71 (d, C**H**, 1H), 7.45 (t, C**H**, 1H), 6.95 (d, C**H**, 1H), 6.88 (t, C**H**, 1H), 2.61 (s, C**H**$_3$, 3H). Mass spectrum: *m/z* (relative intensities) 136 (68), 121 (100), 107 (1), 93 (42), 89 (2), 77 (8), 74 (3), 65 (51), 63 (26), 60 (5), 53 (14), 51 (8), 50 (12), 43 (39), 39 (49). The ^{1}H NMR and MS results are in agreement with those reported in a reference database.[17] DSC (fusion, β = 1 or 2 K·min^{-1}, m = 3−20 mg): T_{on} = 278.50 ± 0.02 K, T_{max} = 281.15 ± 1.02 K, and $\Delta_{fus}H_m^o$ = 13.0 ± 0.1 kJ·mol^{-1}. The obtained T_{on} is 2.8 K higher than the previously reported T_{fus} = 275.7 K.[15]

2-Hydroxybenzamide. 2HBM (Aldrich, 99%) was purified by sublimation at 368 K and 1.0 Pa. The obtained sample was stored in a Schlenk tube under N_2 atmosphere prior to use. Elemental analysis for $C_8H_8O_2$: expected C 61.31%, H 5.17%, N 10.21%; found C 61.28%, H 5.47%, N 9.84% (average of two determinations). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.18 (s, O**H**, 1H), 7.43 (s, C**H**, 1H), 7.38 (d, C**H**, 1H), 7.00 (d, C**H**, 1H), 6.88 (s, C**H**, 1H), 6.16 (s, N**H**, 1H), 5.93 (s, N**H**, 1H). The ^{1}H NMR results are in agreement with those reported in a reference database.[17] No impurities were detected by GC−MS. The obtained powder pattern matched that calculated from the published unit cell dimensions of a monoclinic phase (space group $I2/a$, a = 12.901 Å, b = 4.982 Å, c = 20.987 Å, β = 91.50°)[19,20] using the program Mercury 1.1.2[21] (see Supporting Information for details). DSC (fusion, one experiment, β = 10 K·min^{-1}, m = 3 mg): T_{on} = 413.2 K, T_{max} = 414.2 K, and $\Delta_{fus}H_m^o$ = 27.1 kJ·mol^{-1}. The indicated T_{on} and T_{max} are in good agreement with the value T_{fus} = 414 K obtained by Grady et al.[22] but are higher than T_{fus} = 411.9 ± 0.5 K given by Nordström and Rasmunson.[23] The latter authors also reported $\Delta_{fus}H_m^o$ = 29.0 ± 0.3 kJ·mol^{-1}.

4-Hydroxybenzamide. 4HBM (Aldrich, 98%) was purified by sublimation at 403 K and 1.0 Pa. The obtained sample was stored in a Schlenk tube under N_2 atmosphere prior to use. Elemental analysis for $C_7H_7NO_2$: expected C 61.31%, H 5.17%, N 10.21%; found C 61.27%, H 5.40%, N 10.10% (average of two determinations). ^1H NMR (400 MHz, DMSO): δ 9.95 (s, **O**H, 1H), 7.74 (s, C**H**, 2H) 7.71 (s, N**H**, 1H), 7.08 (s, N**H**, 1H), 6.76 (d, C**H**, 2H). The ^1H NMR results are in agreement with those reported in a reference database.[17] No impurities were detected by GC−MS. The powder pattern was indexed as monoclinic, space group $P2_1/c$, with $a = 4.548(2)$ Å, $b = 8.764(5)$ Å, $c = 15.768(9)$ Å, $\beta = 90.73(4)°$. These values are in good agreement with the previously reported $a = 4.5828(15)$ Å, $b = 8.825(3)$ Å, $c = 15.888(5)$ Å, and $\beta = 90.770(7)°$.[24] DSC (fusion, one experiment, $\beta = 5\ K\cdot min^{-1}$, $m = 3$ mg): $T_{on} = 433.1$ K, $T_{max} = 433.8$ K, and $\Delta_{fus}H^o_m = 25.4\ kJ\cdot mol^{-1}$. These results are in good agreement with the $T_{fus} = 433.2$ K and $\Delta_{fus}H^o_m = 25.2 \pm 0.2\ kJ\cdot mol^{-1}$ given by Perlovich et al.[22]

Combustion Calorimetry. The standard energies of combustion of 2HBA, 2HAP, and 2HBM were measured with an isoperibol stirred liquid combustion macrocalorimeter[25] and those of 4HBA and 4HBM with an isoperibol aneroid combustion microcalorimeter.[26,27]

In the experiments with solid 2HBM, a pellet of the compound with a mass of 0.8−1.0 g was weighed to ±0.01 mg with a Mettler AT201 balance inside a platinum crucible, which was then adjusted to the sample holder in the bomb head. The platinum ignition wire (Johnson Matthey; mass fraction 0.9995; diameter 0.05 mm) was connected between the two discharge electrodes. A cotton thread fuse of empirical formula $CH_{1.887}O_{0.902}$ and standard massic energy of combustion $\Delta_c u° = -16565.9 \pm 8.6\ J\cdot g^{-1}$,[25] was also weighed to ±0.01 mg in the Mettler AT201 balance. One end of the fuse was tied to the ignition wire and the other was brought into contact with the pellet. A volume of 1.0 cm^3 of distilled and deionized water from a Millipore system (conductivity, <0.1 $\mu S\cdot cm^{-1}$) was added to the bomb body by means of a volumetric pipet. The stainless-steel bomb (Parr 1108) of 340 cm^3 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. The combustion of the sample was initiated by discharge of a 2990 μF capacitor, from a potential of 40 V, through the platinum wire. The discharge current heated the wire and when the temperature was increased sufficiently the thread fuse ignited, and the combustion propagated to the sample material. The procedure used to study the liquids 2HBA and 2HAP was similar. In these cases the samples were sealed inside a Melinex bag of massic energy of combustion $\Delta_c u° = -22902 \pm 5\ J\cdot g^{-1}$,[28] which was also weighed to ±0.01 mg with the Mettler AT201 balance. To attain a controlled and complete combustion, it was necessary to reduce the oxygen pressure inside the bomb to 2.53 MPa. The nitric acid formed in all macro calorimetric experiments from combustion of the sample or traces of atmospheric N_2 remaining inside the bomb after purging, was determined by titration with aqueous sodium hydroxide (Merck titrisol, 0.01 $mol\cdot dm^{-3}$), using methyl red as indicator. The energy equivalent of the calorimeter, $\epsilon° = 18566.22 \pm 1.26\ J\cdot K^{-1}$, was obtained from the combustion of benzoic acid (BA; NIST SRM 39j), whose massic energy of combustion under the certificate conditions was $\Delta_c u(\text{BA,cert}) = -26434 \pm 3\ J\cdot g^{-1}$. The $\epsilon°$ value refers to 3751.99 g of distilled water inside the calorimeter proper.

In the microcalorimetry experiments with 4HBA a pellet of the sample with a mass of 20−55 mg was weighed to 0.1 μg in a Sartorius 4504 Mp8-1 ultramicrobalance inside a platinum crucible. The crucible with the sample was transferred to the sample holder in the bomb head. A volume of 50 μL of distilled and deionized water was introduced into the bomb body. The stainless-steel bomb of 17.95 cm^3 internal volume was closed 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 filled with oxygen at a pressure of 3.04 MPa and introduced in the calorimeter proper. The ignition of the sample was initiated by discharge of a 2200 μF capacitor from a potential of 40 V through a platinum wire. The energy equivalent of the apparatus, $\epsilon° = 1894.66 \pm 0.30\ J\cdot K^{-1}$, was determined with the same benzoic acid sample (NIST SRM 39j) used to calibrate the macrocalorimeter. A similar procedure was followed in the experiments with 4HBM, where the sample mass was in the range 16−28 mg. To attain complete combustion, the sample was burned under 3.14 MPa of O_2 and a drop (ca. 2−7 mg) of *n*-hexadecane (Aldrich 99+), weighed to 0.1 μg, was added to the crucible as combustion aid. Two batches of *n*-hexadecane were used. The corresponding standard massic energies of combustion had been previously determined in our laboratory by combustion macro calorimetry as $\Delta_c u° = -47177.3 \pm 1.5\ J\cdot g^{-1}$ and $\Delta_c u° = -47185.4 \pm 1.6\ J\cdot g^{-1}$. The energy equivalent of the apparatus, $\epsilon° = 1895.27 \pm 0.33\ J\cdot K^{-1}$, was obtained from calibration with benzoic acid (BDH thermochemical standard), whose massic energy of combustion under certificate conditions was $\Delta_c u(\text{BA,cert}) = -26433 \pm 2\ J\cdot g^{-1}$. The HNO_3 formed in all micro calorimetry experiments was determined as NO_3^-, using a Dionex 4000i ion chromatography apparatus.

Calvet Drop-Calorimetry. The enthalpies of vaporization of 2HBA and 2HAP, and the enthalpies of sublimation of 4HBA, 2HBM, and 4HBM were determined by using the Calvet drop-microcalorimeter and the experimental procedures previously reported.[29−31] In the vaporization experiments, the sample with a mass in the range 11.0−25.5 mg (2HBA) or 9.5−20.2 mg (2HAP) was placed into a small glass capillary, closed with Parafilm “M” tape (Pechiney, Chicago, IL). The masses of the capillary, sample, and tape were determined with a precision of 1 μg in a Mettler M5 microbalance. The capillary was equilibrated for ca. 10 min, at 298.15 K, inside a furnace placed above the entrance of the calorimetric cell, whose temperature was also set at 298.15 K. It was subsequently dropped into the cell, under N_2 atmosphere, after removing the Parafilm cover. The sample and reference cells were simultaneously evacuated to 0.13 Pa immediately after dropping and the measuring curve due to the vaporization process was acquired. The corresponding enthalpy was derived from the area of this peak and the calibration constant of the apparatus.

The procedure used in the sublimation experiments, was similar to that described for the vaporization, except that the evacuation of the cells was started after the measuring curve corresponding to the heating of the sample from 298.15 K to the temperature of the calorimetric cell was recorded. The mass ranges and temperatures used in the experiments were 4.3−8.2 mg and 346.4 K (4HBA), 3.0−5.2 mg and 361.9 K (2HBM), and 2.9−4.8 mg and 398.4 K (4HBM).

Knudsen Effusion. The enthalpy of sublimation of 4HBA was also determined by using the Knudsen effusion apparatus and operating procedure previously described.[32−34] The tem-

TABLE 1: Enthalpies ($\text{kJ}\cdot\text{mol}^{-1}$) of Combustion, Formation, Vaporization and Sublimation at 298.15 K

compound	$-\Delta_c H^o_m$	$-\Delta_f H^o_m$(cr,1)	$\Delta_{vap}H^o_m/\Delta_{sub}H^o_m$	$-\Delta_f H^o_m$(g)
2HBA,l	3320.44 ± 2.32	291.6 ± 2.5	53.3 ± 0.3 50.3[a]	238.3 ± 2.5
4HBA,cr	3292.08 ± 1.82	320.0 ± 2.0	99.7 ± 0.4 92.0 ± 1.5[b] 99.0 ± 3.4[c]	220.3 ± 2.0
2HAP,l	3941.33 ± 1.86	350.1 ± 2.1	58.3 ± 0.2	291.8 ± 2.1
4HAP,cr				265.4 ± 1.4[d]
2HBM,cr	3348.30 ± 1.06	406.7 ± 1.4 402.7 ± 2.2[e]	101.9 ± 0.4	304.8 ± 1.5
4HBM,cr	3346.85 ± 1.56	408.1 ± 1.8	129.7 ± 1.6	278.4 ± 2.4
2OHBA,cr				497.3 ± 1.4[f]
4OHBA,cr				480.2 ± 1.5[f]

[a] Calculated from ref 66; see text. [b] Calculated from ref 64; see text. [c] Calculated from ref 65; see text. [d] Reference 67. [e] Reference 55. [f] Reference 10.

perature of the tubular furnace surrounding the brass block containing the three effusion cells was controlled to better than ±0.1 K by a Eurotherm 902P thermostatic unit and a K type thermocouple placed in contact with the inner wall of the furnace. The equilibrium temperature inside the cell was assumed to be identical to the temperature of the brass block. This temperature was measured with a precision of ±0.1 K by a Tecnisis 100 Ω platinum resistance thermometer embedded in the block and connected in a four wire configuration to a Keithley 2000 multimeter. Each cell was initially charged with ca. 0.2 g of sample, and the mass loss during a run was determined to ±0.01 mg with a Mettler AT201 balance.

Computational Details. Density functional theory (DFT)[35] and complete basis set extrapolation (CBS-QB3)[36,37] procedures were applied to predict thermochemical properties of the systems under examination. In the case of the DFT methods full geometry optimizations and frequency predictions were carried out with the B3LYP,[38,39] and B3P86[40,41] hybrid functionals, using the 6-31G(d,p),[42] 6-311+G(d,p),[43] and aug-cc-pVDZ,[44,45] basis sets. The corresponding molecular energies were converted to standard enthalpies at 298.15 K by using zero point energy (ZPE) and thermal energy corrections calculated at the same level of theory. The obtained vibration frequencies and ZPEs were not scaled, unless otherwise stated. The DFT and CBS-QB3 calculations were performed with the Gaussian-03 package.[46] The topological properties of the electron density at selected bond critical points have been evaluated by using the theory of atoms in molecules (AIM),[47] as implemented in the AIM2000 program,[48−50] and the output of B3LYP/6-311+G(d,p) calculations.

Results and Discussion

The 2005 IUPAC recommended standard atomic masses were used in the calculation of all molar quantities.[51]

Enthalpies of Reaction and Formation. The obtained standard specific internal energies of combustion of 2HBA, 4HBA, 2HAP, 2HBM, and 4HBM, at 298.15 K, were $\Delta_c u°(\text{2HBA,l}) = -27179.54 \pm 8.83\ \text{J}\cdot\text{g}^{-1}$, $\Delta_c u°(\text{4HBA,cr}) = -26947.28 \pm 5.26\ \text{J}\cdot\text{g}^{-1}$, $\Delta_c u°(\text{2HAP,l}) = -28930.66 \pm 5.68\ \text{J}\cdot\text{g}^{-1}$, $\Delta_c u°(\text{2HBM,cr}) = -24411.37 \pm 2.10\ \text{J}\cdot\text{g}^{-1}$, and $\Delta_c u°(\text{4HBM,cr}) = -24400.79 \pm 2.40\ \text{J}\cdot\text{g}^{-1}$, respectively (see Supporting Information for details). These results lead to the standard molar enthalpies of combustion, $\Delta_c H^o_m$, in Table 1. The uncertainties assigned to $\Delta_c u°$ are the standard deviations of the mean of six individual results and those of $\Delta_c H^o_m$ represent twice the overall standard deviations of the mean, including the contributions from the calibration with benzoic acid and from the combustion of *n*-hexadecane or Melinex.[52,53] The $\Delta_c H^o_m$ values for 2HBA and 4HBA correspond to reaction 1, that for 2HAP to reaction 2, and those for 2HBM and 4HBM to reaction 3:

$$C_7H_6O_2(\text{l/cr}) + 15/2O_2(\text{g}) \rightarrow 7CO_2(\text{g}) + 3H_2O(\text{l}) \quad (1)$$

$$C_8H_8O_2(\text{l}) + 9O_2(\text{g}) \rightarrow 8CO_2(\text{g}) + 4H_2O(\text{l}) \quad (2)$$

$$C_7H_7NO_2(\text{cr}) + 31/4O_2(\text{g}) \rightarrow 7CO_2(\text{g}) + 7/2H_2O(\text{l}) + 1/2N_2(\text{g}) \quad (3)$$

These standard molar enthalpies of combustion in conjunction with $\Delta_f H^o_m(CO_2,\text{g}) = -393.51 \pm 0.13\ \text{kJ}\cdot\text{mol}^{-1}$[54] and $\Delta_f H^o_m(H_2O,\text{l}) = -285.830 \pm 0.040\ \text{kJ}\cdot\text{mol}^{-1}$[54] lead to the enthalpies of formation of 2HBA(l), 4HBA(cr), 2HAP(l), 2HBM(cr), and 4HBM(cr) indicated in Table 1.

Only the enthalpy of formation of 2-hydroxybenzamide had been previously reported as $\Delta_f H^o_m(\text{2HBM,cr}) = -402.7 \pm 2.2\ \text{kJ}\cdot\text{mol}^{-1}$.[55] This result is in reasonable agreement with the value measured in this work if the combined uncertainties of both determinations are considered (Table 1).

The enthalpy of sublimation of 4HBA was obtained from Knudsen effusion and Calvet-drop microcalorimetry experiments (detailed results are given as Supporting Information). The former involved measurements of the vapor pressure, *p*, as a function of the temperature, *T*, in the range 321−351 K. The values of *p* were calculated from[56,57]

$$p = \frac{m}{At}\left(\frac{2\pi RT}{M}\right)^{1/2}\left(\frac{8r + 3l}{8r}\right)\left(\frac{2\lambda}{2\lambda + 0.48r}\right) \quad (4)$$

where *m* is the mass loss during the time *t*; *A*, *l*, and *r* are the area, the thickness, and the radius of the effusion hole, respectively; *M* is the molar mass of the compound under study; *R* is the gas constant; *T* is the absolute temperature; and *λ* is the mean free path given by[58]

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 p} \quad (5)$$

Here *k* represents the Boltzmann constant and *σ* the collision diameter. The collision diameter of 4HBA(g) was estimated as 605 pm, from the van der Waals volume of the molecule calculated with the GEPOL93 program,[59] based on the molecular structure reported by Iwasaki.[18] The van der Waals radii of carbon (1.70 Å), hydrogen (1.20 Å) and oxygen (1.52 Å) given by Bondi were selected for this calculation.[60] The dimensions of the effusion holes of the three cells simultaneously used in the measurements were $A = 1.6974 \times 10^{-7}\ \text{m}^2$, $r = 2.3246 \times 10^{-4}$ m, $l = 2.09 \times 10^{-5}$ m (cell 1); $A = 4.3984 \times 10^{-7}\ \text{m}^2$, $r = 3.7418 \times 10^{-4}$ m, $l = 2.09 \times 10^{-5}$ m (cell 2); and $A = 1.9644 \times 10^{-7}\ \text{m}^2$, $r = 2.5000 \times 10^{-4}$ m, $l = 2.09 \times 10^{-5}$ m (cell 3).

Because the mean free path in eq 5 is pressure dependent, an iterative method was needed to obtain the vapor pressure of the compound through eqs 4 and 5. As a first approximation, *p* was calculated by ignoring the *λ* dependent term in eq 4. The obtained result was subsequently used to derive *λ* from eq 5. The calculated mean free path was introduced in eq 4 and a second *p* value was calculated. The iteration was continued until the difference between successive values of *p* was smaller than 10^{-8} Pa.

The vapor pressure against temperature data were fitted to eq 6 (Figure 1):[61]

$$\ln p = a + \frac{b}{T} \tag{6}$$

where the slope b is related to the enthalpy of sublimation at the average of the highest and lowest temperatures of the range covered in each series of experiments, T_m, by $\Delta_{sub}H^{o}_{m}(T_m) = -bR$. The obtained results were $a = 34.72 \pm 0.24$, $b = -11823.4 \pm 83.8$, and $\Delta_{sub}H^{o}_{m}(\mathrm{4HBA,342.1K}) = 98.3 \pm 1.5$ $\mathrm{kJ\cdot mol^{-1}}$ (cell 1); $a = 34.46 \pm 0.35$, $b = -11749.6 \pm 116.3$, and $\Delta_{sub}H^{o}_{m}(\mathrm{4HBA,331.4K}) = 97.7 \pm 2.1$ $\mathrm{kJ\cdot mol^{-1}}$ (cell 2); $a = 34.72 \pm 0.213$, $b = -11829.2 \pm 72.3$, and $\Delta_{sub}H^{o}_{m}(\mathrm{4HBA,341.5K}) = 98.4 \pm 1.3$ $\mathrm{kJ\cdot mol^{-1}}$ (cell 3). The uncertainties assigned to a and b are the corresponding standard errors, and that for $\Delta_{sub}H^{o}_{m}(T_m)$ includes Student's factor for 95% confidence level (cell 1, $t = 2.201$ for 12 independent measurements; cell 2, $t = 2.160$ for 14 independent measurements; cell 3, $t = 2.179$ for 13 independent measurements). Correction of the obtained $\Delta_{sub}H^{o}_{m}(T_m)$ values to 298.15 K led to $\Delta_{sub}H^{o}_{m}(\mathrm{4HBA,298.15K}) = 99.7 \pm 1.5$ $\mathrm{kJ\cdot mol^{-1}}$ (cell 1), $\Delta_{sub}H^{o}_{m}(\mathrm{4HBA,298.15K}) = 98.2 \pm 2.1$ $\mathrm{kJ\cdot mol^{-1}}$ (cell 2), and $\Delta_{sub}H^{o}_{m}(\mathrm{4HBA,298.15K}) = 99.8 \pm 1.3$ $\mathrm{kJ\cdot mol^{-1}}$ (cell 3). The correction was made through the equation

$$\Delta_{sub}H^{o}_{m}(298.15\mathrm{K}) = \Delta_{sub}H^{o}_{m}(T) + \int_{T}^{298.15\mathrm{K}} [C^{o}_{p,m}(\mathrm{g}) - C^{o}_{p,m}(\mathrm{cr})]\,\mathrm{d}T \tag{7}$$

where $C^{o}_{p,m}(\mathrm{cr})$ and $C^{o}_{p,m}(\mathrm{g})$ are the standard molar heat capacities of the compound in the crystalline and gaseous states, respectively. The calculation was based on the mean value of the heat capacity of solid 4HBA in the range 298−347 K, $C^{o}_{p,m}(\mathrm{4HBA,cr}) = 172.2 \pm 6.1$ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ (mean of two runs), determined by Calvet-drop microcalorimetry,[30] and on the temperature dependence of the heat capacity of gaseous 4HBA in the range 200−400 K calculated by statistical mechanics,[62] using vibration frequencies obtained by the B3LYP/6-31G(d,p) method and scaled by 0.9608.[63] The $C^{o}_{p,m}(\mathrm{g})$ values (in $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$) were fitted to

$$C^{o}_{p,m}(\mathrm{g}) = aT^2 + bT + c \tag{8}$$

whose coefficients are given in Table 2.

The enthalpy of sublimation of 4HBA measured by Calvet-drop microcalorimetry was $\Delta_{sub}H^{o}_{m}(\mathrm{4HBA,346.4\ K}) = 98.3 \pm 0.5$ $\mathrm{kJ\cdot mol^{-1}}$. Correction of this value to 298.15 K as described for the effusion experiments yielded $\Delta_{sub}H^{o}_{m}(\mathrm{4HBA,298.15\ K}) = 99.8 \pm 0.5$ $\mathrm{kJ\cdot mol^{-1}}$. This result is in excellent agreement with those obtained by Knudsen effusion at the same reference temperature. The weighed mean of the four values determined by both techniques is listed in Table 1.

Two independent values of the enthalpy of sublimation of 4HBA can be computed from the vapor-pressure vs temperature data previously reported: 91.3 ± 1.5 $\mathrm{kJ\cdot mol^{-1}}$ at 334.7 K[64] and 98.2 ± 3.4 $\mathrm{kJ\cdot mol^{-1}}$ at 319.7 K.[65] The corresponding enthalpies of sublimation at 298.15 K, derived as mentioned above, are also indicated in Table 1. We note that although the value based on the results of Parsons et al.[65] is in excellent agreement with the result obtained in this work, the enthalpy of sublimation of 4HBA calculated from the work of Aihara[64] shows a discrepancy of 7.7 $\mathrm{kJ\cdot mol^{-1}}$.

Calvet-drop microcalorimetry was also used to measure the enthalpies of vaporization of 2HBA and 2HAP at 298.15 K indicated in Table 1, and the enthalpies of sublimation of 2HBM and 4HBM at 361.9 and 398.4 K, respectively. It is noted that the $\Delta_{vap}H^{o}_{m}(\mathrm{2HBA,298.15K})$ obtained in this work is 3 $\mathrm{kJ\cdot mol^{-1}}$ higher than the value derived from the vapor pressure data reported by Stull (Table 1).[66] The experiments with the hydroxybenzamides led to $\Delta_{sub}H^{o}_{m}(\mathrm{2HBM,361.9K}) = 101.0 \pm 0.4$ $\mathrm{kJ\cdot mol^{-1}}$ and $\Delta_{sub}H^{o}_{m}(\mathrm{4HBM,398.4K}) = 127.6 \pm 1.6$ $\mathrm{kJ\cdot mol^{-1}}$. Correction of these results to 298.15 K by using eq 7, led to the values indicated in Table 1. The corrections were based on $C^{o}_{p,m}(\mathrm{2HBM,cr}) = 178.3 \pm 2.7$ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ (mean of three determinations in the range 298−362 K) and $C^{o}_{p,m}(\mathrm{4HBM,cr}) = 196.1 \pm 6.9$ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ (mean of three determinations in the range 298−399 K), and on the corresponding heat capacities in the gaseous state. These were calculated through eq 8 using the parameters listed in Table 2. The temperature dependences of the heat capacities of gaseous 2HBM and 4HBM in the range 200−400 K were calculated by Statistical Mechanics,[62] as above-described for 4HBA.

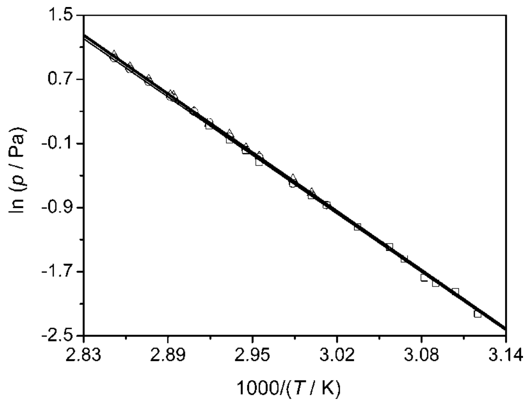


Figure 1. Vapor pressure of 4-hydroxybenzaldehyde as a function of the temperature: (△) cell 1; (□) cell 2; (○) cell 3.

TABLE 2: Coefficients of Eq 8

	-10^4a	b	$-c$
4HBA	2.64	0.541	6.37
2HBM	3.57	0.661	15.5
4HBM	3.65	0.660	9.92

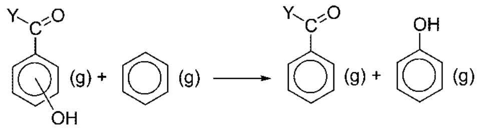
The $\Delta_fH^{o}_{m}(\mathrm{cr/l})$ and $\Delta_{sub}H^{o}_{m}/\Delta_{vap}H^{o}_{m}$ determined in this work lead to the enthalpies of formation of 2HBA, 4HBA, 2HAP, 2HBM, and 4HBM in the gaseous state indicated in Table 1. Also included in Table 1 are the $\Delta_fH^{o}_{m}(\mathrm{g})$ values at 298.15 K previously obtained in our laboratory for 4′-hydroxyacetophenone (4HAP),[67] 2-hydroxybenzoic acid (2OHBA),[10] and 4-hydroxybenzoic acid (4OHBA).[10] This set of data in conjunction with $\Delta_fH^{o}_{m}(\mathrm{C_6H_6,g}) = 82.6 \pm 0.7$ $\mathrm{kJ\cdot mol^{-1}}$,[68] $\Delta_fH^{o}_{m}(\mathrm{C_6H_5OH,g}) = -96.4 \pm 0.9$ $\mathrm{kJ\cdot mol^{-1}}$,[68] $\Delta_fH^{o}_{m}[\mathrm{C_6H_5C(O)H,g}] = -36.7 \pm 2.8$ $\mathrm{kJ\cdot mol^{-1}}$,[68] $\Delta_fH^{o}_{m}[\mathrm{C_6H_5C(O)CH_3,g}] = -86.7 \pm 1.5$ $\mathrm{kJ\cdot mol^{-1}}$,[68] $\Delta_fH^{o}_{m}[\mathrm{C_6H_5C(O)NH_2,g}] = -100.9 \pm 1.2$ $\mathrm{kJ\cdot mol^{-1}}$,[68] and $\Delta_fH^{o}_{m}(\mathrm{C_6H_5COOH,g}) = -294.0 \pm 2.2$ $\mathrm{kJ\cdot mol^{-1}}$[68] allowed the calculation of the enthalpies of the isodesmic reactions 9 and 10 listed in Table 3. Also included in Table 3 are the corresponding values calculated by several theoretical models (see Supporting Information for details). It can be concluded that, in general, the CBS-QB3 method is able to reproduce the experimental enthalpies of reactions 9 and 10 within their uncertainties, the maximum and average absolute deviations being 7.6 and 3.3 $\mathrm{kJ\cdot mol^{-1}}$, respectively. The discrepancies found for the various DFT models are not considerably different (maximum and average deviations in the ranges 7.4−7.6 and 3.5−3.7 $\mathrm{kJ\cdot mol^{-1}}$, respectively), except when reaction 9 involves the ortho isomer. In this case the maximum and average discrepancies increase and the corresponding ranges widen to 6.8−16.9 and 4.7−14.9 $\mathrm{kJ\cdot mol^{-1}}$, respectively. A clear basis set effect is observed because the deviations found for the B3LYP and B3P86 models decrease

TABLE 3: Experimental and Theoretical Enthalpies (kJ·mol^{-1}) of Reactions 9 and 10[a]

Y	Z	B3LYP/ 6-31G(d,p)	B3LYP/ 6-311+G(d,p)	B3LYP/ aug-cc-pVDZ	B3P86/ 6-31G(d,p)	B3P86/ 6-311+G(d,p)	B3P86/ aug-cc-pVDZ	CBS-QB3	experimental
					2-Hydroxybenzoyl				
					Reaction 9				
H		36.2 (13.6)	29.4 (6.8)	30.2 (7.6)	39.5 (16.9)	33.4 (10.8)	34.6 (12.0)	26.9 (4.3)	22.6 ± 3.9
CH_3		37.7 (11.6)	31.4 (5.3)	32.2 (6.1)	41.5 (15.4)	35.9 (9.8)	37.0 (10.9)	28.6 (2.5)	26.1 ± 2.8
NH_2		37.4 (12.5)	30.3 (5.4)	31.6 (6.7)	41.3 (16.4)	35.0 (10.1)	36.5 (11.6)	29.5 (4.6)	24.9 ± 2.2
OH		32.0 (7.7)	25.6 (1.3)	26.2 (1.9)	35.2 (10.9)	29.4 (5.1)	30.4 (6.1)	24.4 (0.1)	24.3 ± 2.9
					Reaction 10				
H	CH_3	−1.5 (2.0)	−2.0 (1.5)	−2.0 (1.6)	−2.0 (1.5)	−2.4 (1.1)	−2.4 (1.1)	−1.8 (1.7)	3.5 ± 4.6
H	NH_2	−1.2 (1.1)	−1.0 (1.4)	−1.3 (1.0)	−1.8 (0.5)	−1.5 (0.8)	−1.9 (0.4)	−2.7 (−0.4)	−2.3 ± 4.2
CH_3	NH_2	0.4 (−0.9)	1.1 (0.1)	0.6 (−0.6)	0.2 (−1.0)	0.9 (−0.3)	0.5 (−0.8)	−0.9 (−2.1)	1.2 ± 2.2
H	OH	4.2 (5.9)	3.8 (5.5)	4.0 (5.7)	4.4 (6.1)	4.1 (5.8)	4.1 (5.8)	2.5 (4.2)	−1.7 ± 4.6
CH_3	OH	5.7 (3.9)	5.8 (4.0)	5.9 (4.1)	6.4 (4.6)	6.5 (4.7)	6.5 (4.7)	4.2 (2.4)	1.8 ± 3.7
NH_2	OH	5.4 (4.8)	4.7 (4.1)	5.3 (4.7)	6.2 (5.6)	5.6 (5.0)	6.1 (5.5)	5.1 (4.5)	0.6 ± 3.2
					4-Hydroxybenzoyl				
					Reaction 9				
H		6.3 (1.7)	5.9 (1.3)	5.9 (1.3)	6.7 (2.1)	6.4 (1.8)	6.4 (1.8)	4.2 (−0.4)	4.6 ± 3.6
CH_3		5.6 (5.9)	5.3 (5.6)	5.3 (5.6)	5.9 (6.2)	5.6 (5.9)	5.6 (5.9)	4.0 (4.3)	−0.3 ± 2.4
NH_2		3.8 (5.3)	3.5 (5.0)	3.6 (5.1)	4.0 (5.5)	3.8 (5.3)	3.8 (5.3)	2.9 (4.4)	−1.5 ± 2.9
OH		5.5 (−1.7)	5.4 (−1.8)	5.3 (−1.9)	5.7 (−1.5)	5.7 (−1.5)	5.7 (−1.5)	4.0 (−3.2)	7.2 ± 2.9
					Reaction 10				
H	CH_3	0.7 (−4.2)	0.6 (−4.3)	0.5 (−4.4)	0.8 (−4.1)	0.8 (−4.1)	0.7 (−4.2)	0.1 (−4.8)	4.9 ± 4.0
H	NH_2	2.5 (−3.7)	2.4 (−3.7)	2.3 (−3.8)	2.7 (−3.5)	2.6 (−3.5)	2.5 (−3.6)	1.3 (−4.8)	6.1 ± 4.4
CH_3	NH_2	1.8 (0.6)	1.8 (0.6)	1.8 (0.6)	1.9 (0.7)	1.9 (0.7)	1.8 (0.6)	1.2 (0.0)	1.2 ± 3.4
H	OH	0.8 (3.4)	0.6 (3.2)	0.5 (3.1)	0.9 (3.5)	0.8 (3.4)	0.7 (3.3)	0.2 (2.8)	−2.6 ± 4.4
CH_3	OH	0.1 (7.6)	−0.1 (7.4)	0.0 (7.5)	0.1 (7.6)	0.0 (7.5)	0.0 (7.5)	0.0 (7.5)	−7.5 ± 3.4
NH_2	OH	−1.7 (7.0)	−1.8 (6.9)	−1.8 (6.9)	−1.7 (7.0)	−1.9 (6.8)	−1.8 (6.9)	−1.1 (7.6)	−8.7 ± 3.8

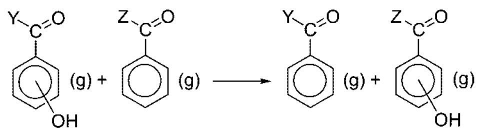
[a] The values in parentheses correspond to the difference between the calculated and experimental values.

by 6−7 kJ·mol^{-1} when the 6-31G(d,p) basis is replaced by the 6-311+G(d,p) basis. This probably reflects the difficulty of the DFT models with smaller basis sets to account for the uncompensated intramolecular H-bond cleavage ongoing from reactants to products. It is also noted that, for the same basis, the predictions of the B3LYP model are closer to the experimental values by ca. 4 kJ·mol^{-1}, than those of the B3P86 functional. Finally, the good general agreement between the experimental and calculated data when the B3LYP/6-311+G(d,p) and CBS-QB3 models are considered supports the reliability of these computational methods and indicates a very good thermodynamic consistency between their estimates and the corresponding experimental values derived from standard enthalpy of formation data.



(9)

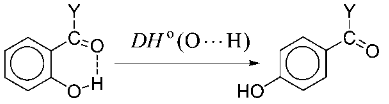
(Y = H, OH, CH_3 and NH_2)



(10)

(Y = H, OH, CH_3 and NH_2; Z = H, OH, CH_3 and NH_2; Y ≠ Z)

Intramolecular O···H Hydrogen Bonding Energetics in 2-HOC$_6$H$_4$C(O)Y. As mentioned in the Introduction the energetics of the 2-HOC$_6$H$_4$C(O)Y isomers is significantly determined by the presence of an intramolecular H-bond involving the phenolic OH group and the CO group of the C(O)Y substituent. Our results allow us to analyze the energetics of this interaction using the ortho-para method.[69] As previously discussed, an intramolecular H-bond is an intrinsic characteristic of the molecule under examination and it is therefore difficult to envision a reaction whose energetics will simply reflect the establishment of that interaction from two separated donor and acceptor precursors. Hence, to evaluate intramolecular bond "strengths" a suitable reference structure or reaction has to be selected. In the ortho−para method 4-HOC$_6$H$_4$C(O)Y is used as reference system for 2-HOC$_6$H$_4$C(O)Y, because it is generally agreed that the electronic effects of ortho and para substituents on the molecular energetics are comparable.[70−73] The intramolecular hydrogen bond dissociation enthalpies, $DH°(O\cdots H)$, for 2-HOC$_6$H$_4$C(O)Y compounds are therefore identified with the enthalpy of reaction 11:



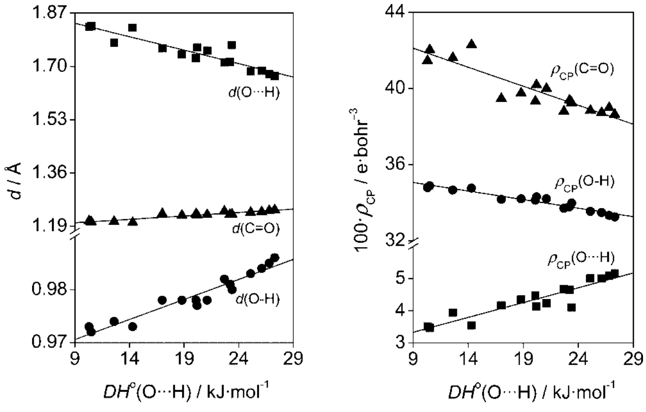
(11)

The values of $DH°(O\cdots H)$ derived for 2-HOC$_6$H$_4$C(O)Y (Y = H, CH_3, NH_2, OH), from experimental $\Delta_f H^o_m(g)$ values, or computed H^o_m data obtained in this work using the B3LYP/6-311+G(d,p) and CBS-QB3 methods are listed in Table 4 (details of the theoretical results are given as Supporting Information). It can be concluded from Table 4 that the agreement between the experimental and computed H-bond dissociation enthalpies is very good. Because the B3LYP/6-311+G(d,p) method yields essentially the same values of $DH°(O\cdots H)$ as the CBS-QB3 model, with considerably less computational effort, it was further applied to Y = $CH_2CH{=}CH_2$, C≡CH, CH_2F, $NHCH_3$, NO_2, OCH_3, OCN, CN, F, Cl, SH, and SCH_3.

TABLE 4: Experimental and Theoretical Hydrogen Bond Dissociation Enthalpies, $DH°(O\cdots H)$, in $2\text{-}HOC_6H_4C(O)Y$ Compounds Obtained by the Ortho−Para Method ($kJ\cdot mol^{-1}$); Calculated Interatomic Distances, d (Å)[a] and Electron Densities at the Bond Critical Point, ρ_{cp} ($e\cdot bohr^{-3}$)[b] for Selected Bonds; Differences, $\Delta\tilde{\nu}(O-H)$, between the O−H Stretching Frequencies in $4\text{-}HOC_6H_4C(O)Y$ and $2\text{-}HOC_6H_4C(O)Y$ (cm^{-1});[a] and Substituent Parameters for Inductive, F, and Resonance, R Effects[c]

	$DH°(O\cdots H)$			$O\cdots H$		O−H		C=O				
Y	experimental	CBS-QB3	B3LYP/6-311+G(d,p)	d	$100\rho_{cp}$	d	$100\rho_{cp}$	d	$100\rho_{cp}$	$\Delta\tilde{\nu}(O-H)$	F	R
NO_2			10.3	1.826	3.51	0.977	34.79	1.207	41.45	253.8	0.65	0.13
OCN			10.5	1.829	3.47	0.976	34.88	1.204	42.03	238.7	0.69	0.15
Cl			12.6	1.775	3.94	0.978	34.66	1.205	41.61	221.8	0.42	−0.19
F			14.3	1.823	3.54	0.977	34.76	1.202	42.28	267.2	0.45	−0.39
CN			17.0	1.758	4.17	0.982	34.17	1.230	39.46	365.4	0.51	0.15
SH			18.8	1.738	4.35	0.982	34.20	1.225	39.75	366.5	0.30	−0.15
SCH_3			20.1	1.727	4.47	0.982	34.13	1.229	39.32	383.6	0.23	−0.23
OH	17.1 ±2.1[d]	20.4	20.2	1.760	4.13	0.981	34.30	1.226	40.18	355.0	0.33	−0.70
OCH_3			21.1	1.750	4.24	0.982	34.20	1.227	39.99	368.4	0.29	−0.56
C≡CH			22.7	1.713	4.67	0.986	33.7	1.238	38.79	448.9	0.22	0.01
CH_2F			23.2	1.714	4.65	0.985	33.79	1.228	39.38	437.4	0.15	−0.04
H	18.0 ± 3.2	22.7	23.4	1.768	4.10	0.984	33.98	1.228	39.24	407.5	0.03	0.00
$CH_2CH{=}H_2$			25.1	1.684	5.01	0.987	33.54	1.234	38.84	483.0	−0.06	−0.08
CH_3	26.4 ± 2.5	24.6	26.1	1.686	5.00	0.988	33.48	1.236	38.73	495.0	0.01	−0.18
NH_2	26.4 ± 2.5	26.7	26.8	1.675	5.09	0.989	33.33	1.240	38.98	512.7	0.08	−0.74
$NHCH_3$			27.3	1.670	5.16	0.990	33.25	1.243	38.63	527.4	0.03	−0.73

[a] Calculated by the B3LYP/6-311+G(d,p) method. [b] Calculated using the theory of atoms in molecules, based on data obtained at the B3LYP/6-311+G(d,p) level of theory (see text). [c] From ref 74. [d] From experimental data in ref 10.



(a) (b)

Figure 2. (a) Interatomic distances, d, and (b) electron densities at the bond critical point, ρ_{cp} against $DH°(O\cdots H)$ for $2\text{-}HOC_6H_4C(O)Y$ (Y = H, CH_3, $CH_2CH{=}CH_2$, C≡CH, CH_2F, NH_2, $NHCH_3$, NO_2, OH, OCH_3, OCN, CN, F, Cl, SH, and SCH_3) compounds.

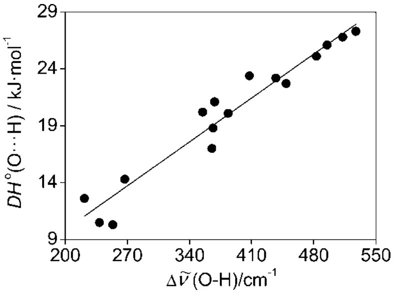


Figure 3. Differences, $\Delta\tilde{\nu}(O-H)$, between the O−H stretching frequencies in $4\text{-}HOC_6H_4C(O)Y$ and $2\text{-}HOC_6H_4C(O)Y$ against $DH°(O\cdots H)$ for Y = H, CH_3, $CH_2CH{=}CH_2$, C≡CH, CH_2F, NH_2, $NHCH_3$, NO_2, OH, OCH_3, OCN, CN, F, Cl, SH, and SCH_3.

Also included in Table 4 are some selected interatomic distances, d, calculated by the B3LYP/6-311+G(d,p) method and the corresponding AIM electron densities at the bond critical point, ρ_{cp}, along with the differences $\Delta\tilde{\nu}(O-H)$, between the O−H stretching frequencies in $4\text{-}HOC_6H_4C(O)Y$ and $2\text{-}HOC_6H_4C(O)Y$, calculated by the B3LYP/6-311+G(d,p) method.

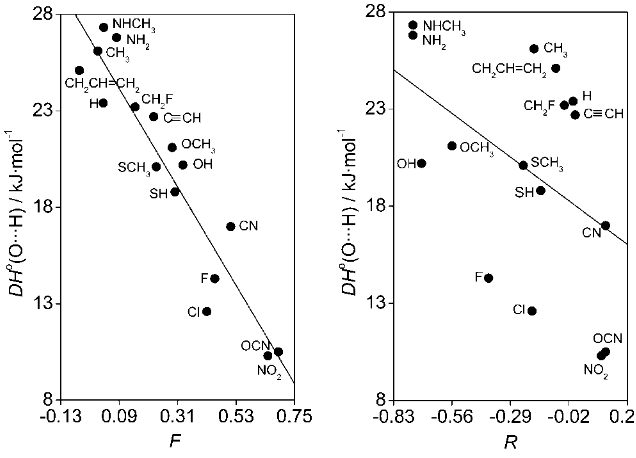
The usefulness of correlating hydrogen bond dissociation enthalpies with structural and spectroscopic data has long been recognized.[5,6] Plots of d and ρ_{cp}, respectively, against the $DH°(O\cdots H)$ values obtained from the B3LYP/6-311+G(d,p) results are illustrated in Figure 2. It can be concluded from Figure 2a that, in general, as $DH°(O\cdots H)$ increases $d(O\cdots H)$ tends to decrease, and both $d(O-H)$ and $d(C{=}O)$ tend to increase. These trends are consistent with what should be expected for the formation of hydrogen bonds of increasing strength, and are also in agreement with the corresponding increase of $\rho_{cp}(O\cdots H)$ and the decreases of $\rho_{cp}(O-H)$ and $\rho_{cp}(C{=}O)$ apparent in Figure 2b.

The magnitude of the shift between the infrared stretching frequency of a "free" O−H bond in a reference structure and a O−H bond involved in hydrogen bonding has also used as a valuable measure of the corresponding hydrogen bond strength.[5,6] The result of a linear least-squares fit to the $DH°(O\cdots H)$ and $\Delta\tilde{\nu}(O-H)$ values in Table 4 is illustrated in Figure 3, and corresponds to

$$DH°(O\cdots H) = (0.055 \pm 0.004)\Delta\tilde{\nu}(O-H) - (1.2 \pm 1.5) \tag{12}$$

This equation, with a regression coefficient $R = 0.97$ and a standard error $\sigma = 1.42$, reproduces the $DH°(O\cdots H)$ values in Table 4 with maximum and average deviations of 2.5 and 1.1 $kJ\cdot mol^{-1}$, respectively.

A dependence of $DH°(O\cdots H)$ on the nature of the substituent Y is clearly apparent in Table 4. This had also been noted by other authors, for hydrogen bond strengths derived from the difference in energy between the most stable structure of a given $2\text{-}HOC_6H_4C(O)Y$ compound and that of the corresponding tautomer with the O−H group rotated by 180° around the C−O axis, both calculated at the HF/3-21G,[7] HF/6-31G(d,p),[7] or B3LYP/6-31G(d,p)[7−9] levels of theory. It is worth noting that for hydroxybenzoyl compounds this so-called cis−trans method, whose differences relative to the ortho−para scheme were discussed in a previous publication,[69] typically leads to $DH°(O\cdots H)$ values which are ~2.5 times larger than those obtained in this work. Catalán, Palomar and Paz[74,75] found that



(a) (b)

Figure 4. $DH°(O\cdots H)$ values obtained in this work by the B3LYP/6-311+G(d,p) method for $2\text{-}HOC_6H_4C(O)Y$ compounds as a function of (a) the inductive, F, parameters and (b) resonance, R, parameters of the substituents Y.

TABLE 5: O−H Bond Dissociation Enthalpies ($kJ \cdot mol^{-1}$) for 2- and 4-Hydroxybenzoyl Compounds Relative to Phenol, at 298.15 K

	$DH°(O-H) - DH°(C_6H_5O-H)$	
Y	$2\text{-}HOC_6H_4C(O)Y$	$4\text{-}HOC_6H_4C(O)Y$
NO_2	39.7	22.3
OCN	47.4	21.2
Cl	46.3	17.2
F	49.2	16.7
CN	49.2	18.0
SH	36.3	11.0
SCH_3	37.4	7.7
OH	27.3	10.6
OCH_3	48.9	8.0
C≡CH	49.6	10.2
CH_2F	28.6	11.3
H	36.7	9.9
$CH_2CH{=}CH_2$	36.5	7.9
CH_3	38.3	7.6
NH_2	14.6	6.2
$NHCH_3$	12.8	4.2

in the series Y = H, CH_3, NH_2, $NHCH_3$, OH, OCH_3, F, Cl, SH, and SCH_3, the observed trends could be adequately described by an equation linearly relating the H-bond strengths with the inductive and resonance effects of the substituents, as measured by Taft and Topsom's σ_F and σ_R parameters,[76] respectively. The authors noted that the resonance acceptors CN and NO_2 markedly deviated from the correlation and in the case of Y = NH_2, $NHCH_3$, OH, SH, and SCH_3 used bond strengths corrected for reorganization effects associated with the 180° rotation of the O−H group. From the obtained results they concluded that the inductive effect of the substituent was dominant, and that the bond strength increased with a decreasing electron withdrawing ability of the substituent by inductive effect and an increasing electron donating ability of the substituent through resonance. The predominance of the inductive effect in determining the H-bond dissociation enthalpy trends observed in this work is also supported by the results in Figure 4, which evidence a much better correlation of $DH°(O\cdots H)$ with the inductive (F) parameters recommended by Hansch, Leo and Taft[74] than with the corresponding resonance (R) parameters (Table 4). A linear least-squares fit to the $DH°(O\cdots H)$ and F data in Table 4 gives

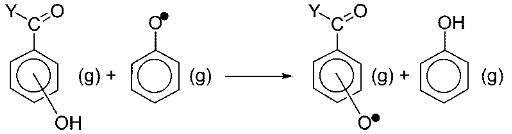
$$DH°(O\cdots H) = -(23.2 \pm 2.2)F + 26.2 \pm 0.8 \quad (13)$$

Equation 13 with a correlation coefficient $R = 0.94$ and $\sigma = 1.96$ reproduces the $DH°(O\cdots H)$ values in Table 4 with a mean deviation of 1.6 $kJ \cdot mol^{-1}$ and a maximum deviation of 3.9 $kJ \cdot mol^{-1}$. No significant statistical gain is obtained when a biparametric relation with F and R is considered. A multiple linear regression analysis to the $DH°(O\cdots H)$, F, and R data in Table 4 leads to

$$DH°(O\cdots H) = -(22.0 \pm 2.3)F - (2.4 \pm 1.7)R + 25.4 \pm 1.0 \quad (14)$$

Equation 14 has $R = 0.95$ and $\sigma = 1.89$ and reproduces the $DH°(O\cdots H)$ values in Table 4 with a mean deviation of 1.5 $kJ \cdot mol^{-1}$ and a maximum deviation of 4.0 $kJ \cdot mol^{-1}$. Comparison of eqs 13 and 14 through an F test[77,78] leads to a calculated value $F_{calc} = 1.31$, which is considerably smaller than the tabulated $F_{table} = 4.67$ for a 95% confidence interval and 13 degrees of freedom.[15] Thus, at least within the framework of the model selected in this work, there seems to be no substantial advantage in considering resonance contributions for the empirical estimation of $DH°(O\cdots H)$ values in $2\text{-}HOC_6H_4C(O)Y$ compounds.

O−H Bond Disssociation Enthalpies. The differences in the O−H bond dissociation enthalpies for the 2- and 4-hydroxybenzoyl compounds studied in this work relative to that in phenol, $DH°(O-H) - DH°(C_6H_5O-H)$, were estimated from the enthalpies of reaction 15, at 298.15 K, computed by the B3LYP/6-311+G(d,p) method (details of the calculations are given as Supporting Information). The obtained values are indicated in Table 5. These differences rather than the absolute values of $DH°(O-H)$ were derived, because there is currently no consensus regarding the "best" value for $DH°(C_6H_5O-H)$, with the recommended data spanning a range of ca. 16 $kJ \cdot mol^{-1}$ (361−377 $kJ \cdot mol^{-1}$).[3,79−82]



(15)

Table 5 shows that $DH°(O-H) - DH°(C_6H_5O-H)$ is systematically larger for 2-hydroxybenzoyl than for the corresponding 4-hydroxybenzoyl isomers. The observed differences reflect the interplay of three effects: (i) the stabilization of all precursor $2\text{-}HOC_6H_4C(O)Y$ molecules relative to their $4\text{-}HOC_6H_4C(O)Y$ counterparts through the intramolecular O···H hydrogen bond discussed in the previous paragraph; (ii) except for Y = OH, NH_2, $NHCH_3$, and CH_2F, the destabilization of the $2\text{-}{}^{\bullet}OC_6H_4C(O)Y$ radicals relative to the corresponding 4-analogues, due to a steric repulsion between the adjacent C(O)Y and $O^{\bullet}$ substituents; (iii) in the case of Y = OH, NH_2, $NHCH_3$, and CH_2F the stabilization of the 2- relative to the $4\text{-}{}^{\bullet}OC_6H_4C(O)Y$ radicals due to the formation of an intramolecular hydrogen bond involving Y and $O^{\bullet}$ (Figure 5), weaker than that in the precursor molecules (see below). This can be rationalized with the aid of Scheme 1, from which it can be deduced that the relationship between the O−H bond dissociation enthalpies in 2-hydroxybenzoyl, $DH°(O-H)_2$, and 4-hydroxybenzoyl, $DH°(O-H)_4$, isomers is given by

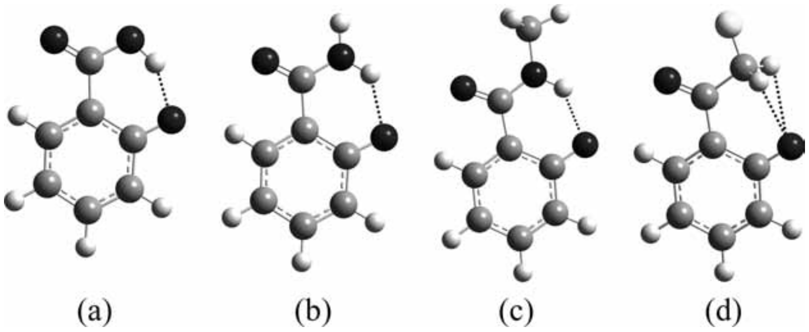


Figure 5. Molecular structures of the 2-$^\bullet OC_6H_4C(O)Y$ radicals calculated at the B3LYP/6-311+G(d,p) level of theory for (a) Y = OH, (b) Y = NH_2, (c) Y = $NHCH_3$, and (d) Y = CH_2F.

SCHEME 1

$$\begin{tikzcd}
\text{2-}HOC_6H_4C(O)Y\ (g) \arrow[r, "DH^\circ(O{-}H)_2"] \arrow[d, "DH^\circ(O\cdots H)"'] & \text{2-}^\bullet OC_6H_4C(O)Y\ (g) + H^\bullet(g) \arrow[d, "\Delta H^\circ_1"] \\
\text{4-}HOC_6H_4C(O)Y\ (g) \arrow[r, "DH^\circ(O{-}H)_4"] & \text{4-}^\bullet OC_6H_4C(O)Y\ (g) + H^\bullet(g)
\end{tikzcd}$$

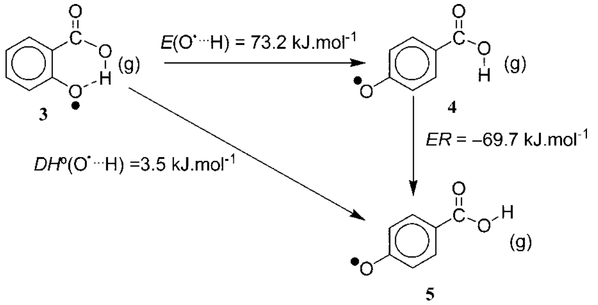
TABLE 6: Values of the Terms in Eq 6 and Tilt angles Between the Planes of the Aromatic Ring and the C(O)Y Group in the 2- (φ_2) and 4-Isomers (φ_4) of the $^\bullet OC_6H_4C(O)Y$ Radicals (Thermodynamic Data in kJ·mol^{-1} and Angles in Degrees)

Y	$DH^\circ(O-H)_2 - DH^\circ(O-H)_4$	$DH^\circ(O\cdots H)$	ΔH°_1	φ_2	φ_4
$NHCH_3$	8.6	27.3	18.7	0	25.3
NH_2	8.4	26.8	18.4	0	24.4
CH_2F	17.3	23.2	5.9	0.1	0
OH	16.7	20.2	3.5	0	0
H	26.8	23.4	−3.4	0	0
$CH_2CH{=}CH_2$	28.6	25.1	−3.5	19.8	3.3
CH_3	30.7	26.1	−4.6	0.3	0
SH	25.3	18.8	−6.5	0	0
NO_2	17.4	10.3	−7.1	26.1	2.1
SCH_3	29.7	20.1	−9.6	0	0
CN	31.2	17.0	−14.2	3.5	0
OCN	26.2	10.5	−15.7	25.7	0
Cl	29.1	12.6	−16.5	34.5	0
$C{\equiv}CH$	39.4	22.7	−16.7	19.8	0
F	32.5	14.3	−18.2	22.0	0
OCH_3	40.9	21.1	−19.8	36.3	0

$$DH^\circ(O-H)_2 - DH^\circ(O-H)_4 = DH^\circ(O\cdots H) - \Delta H^\circ_1 \tag{16}$$

In Scheme 1 and eq 16, $DH^\circ(O\cdots H)$ corresponds to the hydrogen bond enthalpy in the 2-$HOC_6H_4C(O)Y$ compounds, obtained by the ortho−para method (Table 4). For Y = OH, NH_2, $NHCH_3$, and CH_2F, ΔH°_1 represents the hydrogen bond dissociation enthalpy in the 2-$^\bullet OC_6H_4C(O)Y$ radicals derived by the ortho−para method and for the remaining derivatives corresponds to the enthalpic change associated with the release of the steric constraints involving the adjacent C(O)Y and $O^\bullet$ substituents on going from 2- to 4-$^\bullet OC_6H_4C(O)Y$. The values of the various terms in eq 16 are summarized in Table 6, where it is observed that, consistent with the above interpretations, the ΔH°_1 values are positive for cases were the Y substituents in the radical are involved in hydrogen bonding and negative for the remaining substituents. Thus, the presence of an intramolecular H-bond in the precursor molecule combined with the steric interaction between the adjacent C(O)Y and $O^\bullet$ substituents contribute to increase $DH^\circ(O-H)$ in 2-$HOC_6H_4C(O)Y$ relative to the corresponding 4-isomer. The observed difference is, however, smaller when an intramolecular H-bond is present in the radical formed by cleavage of the O−H bond such as in the case of Y = OH, NH_2, $NHCH_3$, and CH_2F.

SCHEME 2



From the ΔH°_1 values in Table 6 it is concluded that $DH^\circ(O^\bullet\cdots H)$ = 3.5 kJ·mol^{-1} (Y = OH), 18.4 kJ·mol^{-1} (Y = NH_2), 18.7 kJ·mol^{-1} (Y = $NHCH_3$), and 5.9 kJ·mol^{-1} (Y = CH_2F). The fact that $DH^\circ(O^\bullet\cdots H)$ is considerably smaller for Y = CH_2F than for Y = NH_2 or Y = $NHCH_3$ seems reasonable. As shown in Figure 5, the 2-$^\bullet OC_6H_4C(O)CH_2F$ radical exhibits two $CH\cdots O^\bullet$ H-bonds, which are expected to be considerably weaker than the $NH\cdots O^\bullet$ bonds present in 2-$^\bullet OC_6H_4C(O)NH_2$ and 2-$^\bullet OC_6H_4C(O)NHCH_3$ radicals.[5,6] This is also consistent with the corresponding electron densities at the bond critical point obtained through AIM calculations, namely $DH^\circ(O^\bullet\cdots H)$ = 0.014 e·bohr^{-3} (Y = CH_2F), 0.028 e·bohr^{-3} (Y = NH_2), 0.030 e·bohr^{-3} (Y = $NHCH_3$), and bond distances $d(O^\bullet\cdots H)$ = 2.509 Å (Y = CH_2F), 1.937 Å (Y = NH_2), 1.916 Å (Y = $NHCH_3$). The value of $DH^\circ(O^\bullet\cdots H)$ = 3.5 kJ·mol^{-1} obtained for 2-$^\bullet OC_6H_4C(O)OH$ seems, however, abnormally low, considering the nature of the H-bond involved. Apparently, this is also in contrast with the fact that for Y = OH, $DH^\circ(O^\bullet\cdots H)$ = 0.045 e·bohr^{-3} is larger and $d(O^\bullet\cdots H)$ = 1.726 Å is shorter than for the radicals with Y = CH_2F, NH_2, and $NHCH_3$, although this line of reasoning should be cautiously applied because bonds of different natures are being considered. The origin of this apparent contradiction was previously addressed by us in the context of a comparative study of structure-energetics relationships in the 2-OHBA and cathecol systems.[10] The ortho → para reaction associated with $DH^\circ(O^\bullet\cdots H)$ can be decomposed into the two steps shown in Scheme 2, where structures 3 and 5 represent the most stable conformers of the 2- and 4-carboxyphenoxyl radicals. Structure 4 is analogous to structure 5 but was built with the same bond distances and angles of structure 3 by moving the $O^\bullet$ substituent to the para position. The corresponding enthalpy was calculated by adding the zero point energy and thermal corrections of structure 5 to the electronic energy obtained from a single point calculation at the B3LYP/6-311+G(d,p) level of theory. Hence, the first step in Scheme 2 corresponds to an "intrinsic" H-bond enthalpy, $E(\mathrm{O}^{\bullet}\cdots\mathrm{H}) = 73.2\ \mathrm{kJ \cdot mol^{-1}}$, which is considerably larger than $DH°(\mathrm{O}^{\bullet}\cdots\mathrm{H})$; the second one, however, involves a negative reorganization energy $ER = -69.7\ \mathrm{kJ \cdot mol^{-1}}$, which significantly contributes to decrease $DH°(\mathrm{O}^{\bullet}\cdots\mathrm{H})$ relative to $E(\mathrm{O}^{\bullet}\cdots\mathrm{H})$. When the same approach is applied to Y = CH_2F, NH_2, $NHCH_3$, the following results are obtained: $E(\mathrm{O}^{\bullet}\cdots\mathrm{H}) = 43.1\ \mathrm{kJ \cdot mol^{-1}}$ and $ER = -37.2\ \mathrm{kJ \cdot mol^{-1}}$ (Y = CH_2F); $E(\mathrm{O}^{\bullet}\cdots\mathrm{H}) = 57.2\ \mathrm{kJ \cdot mol^{-1}}$ and $ER = -38.8\ \mathrm{kJ \cdot mol^{-1}}$ (Y = NH_2); and $E(\mathrm{O}^{\bullet}\cdots\mathrm{H}) = 57.0\ \mathrm{kJ \cdot mol^{-1}}$ and $ER = -38.3\ \mathrm{kJ \cdot mol^{-1}}$ (Y = $NHCH_3$). It should also be noted that although for Y = OH and CH_2F the C(O)Y group is coplanar with the aromatic ring both for the ortho and para isomer, in the case of Y = NH_2, $NHCH_3$ coplanarity is observed in the ortho isomer (due to the intermolecular H-bond) but the para isomer exhibits a tilt angle of 25° (Table 6). This tilt, which is originated by the repulsive interaction between the NH_2 or $NHCH_3$ substituents and the ring system, leads to a destabilization of the para radical thus contributing to further increase $DH°(\mathrm{O}^{\bullet}\cdots\mathrm{H})$ relative to Y = OH and CH_2F.

In the case of the non-hydrogen bonded substituents Y = H, CH_3, $CH_2CH{=}CH_2$, $C{\equiv}CH$, NO_2, OCH_3, OCN, CN, F, Cl, SH, and SCH_3 Table 6 shows a general tendency toward negative $\Delta H°_1$ values with the increase of the difference between the tilt angles of the planes containing the aromatic ring and the C(O)Y group.

Acknowledgment. This work was supported by Fundação para a Ciência e a Tecnologia, Portugal. A grant from Fundação para a Ciência e a Tecnologia (SFRH/BD/12329/2003) is gratefully acknowledged by C.E.S.B. We also thank Dr. H. P. Diogo (IST, Portugal) for the use of the combustion calorimeters in his laboratory and for the DSC analysis of 2- and 4-hydroxybenzamide; Dr. C. Oliveira (IST, Portugal) for the mass spectrometric analysis; Dr. J. M. Nogueira (FCUL, Portugal) for the GC−MS analysis; and Drs. F. Martins (FCUL, Portugal) and R. M. Borges dos Santos (Un. Algarve) for helpful discussions.

Supporting Information Available: Tables S1 and S2 and Figure S1 with the details of the powder X-ray diffraction characterization of 4-hydroxybenzaldehyde, 2-hydroxybenzamide, and 4-hydroxybenzamide. Details of the combustion calorimetry (Tables S3−S8) and Calvet-drop calorimetry experiments (Tables S9−S13) experiments. Table S14 containing the experimental vapor pressures of 4-hydroxybenzaldehyde obtained by the Knudsen effusion method. Tables S15 and S16 with the results of the theoretical calculations.This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Suryan, M. M.; Kafafi, S. A.; Stein, M. M. *J. Am. Chem. Soc.* **1989**, *111*, 1423–1429.

(2) Suryan, M. M.; Kafafi, S. A.; Stein, M. M. *J. Am. Chem. Soc.* **1989**, *111*, 4594–4600.

(3) Borges dos Santos, R. M.; Martinho Simões, J. A. *J. Phys. Chem. Ref. Data* **1998**, *27*, 707–739.

(4) Ross, L.; Barclay, C.; Vinqvist, M. R. Phenols as Antioxidants. In *The Chemistry of Phenols*; Rappoport, Z. , Ed.; John Wiley: Chichester, U.K., 2003; pp 839−908..

(5) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman and Co.: San Francisco, 1960.

(6) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.

(7) Lampert, H.; Mikenda, W.; Karpfen, A. *J. Phys. Chem.* **1996**, *100*, 7418–7425.

(8) Catalán, J.; Palomar, J.; de Paz, J. L. G. *J. Phys. Chem. A* **1997**, *101*, 7914–7921.

(9) Palomar, J.; De Paz, J. L. G.; Catalan, J. *J. Phys. Chem. A* **2000**, *104*, 6453–6463.

(10) Pinto, S. S.; Diogo, H. P.; Guedes, R. C.; Costa Cabral, B. J.; Minas da Piedade, M. E.; Martinho Simões, J. A. *J. Phys. Chem. A* **2005**, *109*, 9700–9708.

(11) Lagoa, A. L. C.; Diogo, H. P.; Dias, M. P.; Minas da Piedade, M. E.; Amaral, L. M. P. F.; Ribeiro da Silva, M. A. V.; Martinho Simões, J. A.; Guedes, R. C.; Costa Cabral, B. J.; Schwarz, K.; Epple, M. *Chem. Eur. J.* **2001**, *7*, 483–489.

(12) Mulder, P.; Mozenson, O.; Lin, S. Q.; Bernardes, C. E. S.; Minas da Piedade, M. E.; Santos, A. F. L. O. M.; Ribeiro da Silva, M. A. V.; DiLabio, G. A.; Korth, H. G.; Ingold, K. U. *J. Phys. Chem. A* **2006**, *110*, 9949–9958.

(13) Richard, L. S.; Bernardes, C. E. S.; Diogo, H. P.; Leal, J. P.; Minas da Piedade, M. E. *J. Phys. Chem. A* **2007**, *111*, 8741–8748.

(14) Laugier, J.;Bochu, B. Checkcell; http://www.ccp14.ac.uk/tutorial/lmgp.

(15) Lide, D. R. *Handbook of Chemistry and Physics*, 87th ed.; Taylor and Francis: Boca Raton, FL, 2007.

(16) Heilbron, D. S. O.; Cook, A. H.; Bunbury, H. M.; Hey, D.; Pollock, H. J. R. A.; Stevens, R. *Dictionary of Organic Compounds*; Eyere and Spottiswoode Publishers: London, 1965; Vol. 3.

(17) Saito, T.; Hayamizu, K.; Yanagisawa, M.; Yamamoto, O.; Wasada, N.; Someno, K.; Kinugasa, S.; Tanabe, K.; Tamura, T.; Hiraishi, J. Spectral Data Base for Organic Compounds (SDBS); http://www.aist.go.jp/RIODB.

(18) Iwasaki, F. *Acta Crystallogr.* **1977**, *B33*, 1646–1648.

(19) Pertlik, F. *Monatsh. Chem.* **1990**, *121*, 129–139.

(20) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380–388.

(21) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl. Crystallogr.* **2006**, *39*, 453–457.

(22) Grady, L. T.; Hays, S. E.; King, R. H.; Klein, H. R.; Mader, W. J.; Wyatt, D. K.; Zimmere, R. O. *J. Pharm. Sci.* **1973**, *62*, 456–464.

(23) Nordström, F. L.; Rasmuson, A. C. *J. Chem. Eng. Data* **2006**, *51*, 1775–1777.

(24) Perlovich, G. L.; Hansen, L. K.; Volkova, T. V; Mirza, S.; Manin, A. N.; Bauer-Brandl, A. *Cryst. Growth Des.* **2007**, *7*, 2643–2648.

(25) Pinto, S. S.; Diogo, H. P.; Minas da Piedade, M. E. *J. Chem. Thermodyn.* **2003**, *35*, 177–188.

(26) Diogo, H. P.; Minas da Piedade, M. E. *J. Chem. Thermodyn.* **1995**, *27*, 197–206.

(27) Santos, R. C.; Diogo, H. P.; Minas da Piedade, M. E. *J. Chem. Thermodyn.* **1999**, *31*, 1417–1427.

(28) Skinner, H. A.; Snelson, A. *Trans. Faraday Soc.* **1960**, *56*, 1776–1783.

(29) Kiyobayashi, T.; Minas da Piedade, M. E. *J. Chem. Thermodyn.* **2001**, *33*, 11–21.

(30) Bernardes, C. E. S.; Santos, L. M. N. B. F.; Minas da Piedade, M. E. *Meas. Sci. Technol.* **2006**, *17*, 1405–1408.

(31) Bernardes, C. E. S.; Minas da Piedade, M. E.; Amaral, L. M. P. F.; Ferreira, A. I. M. C. L.; Ribeiro da Silva, M. A. V.; Diogo, H. P.; Costa Cabral, B. J. *J. Phys. Chem. A* **2007**, *111*, 1713–1720.

(32) Calado, J. C. G.; Dias, A. R.; Minas da Piedade, M. E.; Martinho Simões, J. A. *Rev. Port. Quim.* **1980**, *22*, 53–62.

(33) Diogo, H. P.; Minas da Piedade, M. E.; Fernandes, A. C.; Martinho Simões, J. A.; Ribeiro da Silva, M. A. V.; Monte, M. J. S. *Thermochim. Acta* **1993**, *228*, 15–22.

(34) Diogo, H. P.; Minas da Piedade, M. E.; Gonçalves, J. M.; Monte, M. J. S.; Ribeiro da Silva, M. A. V. *Eur. J. Inorg. Chem.* **2001**, *228*, 257–262.

(35) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*, 2nd ed.; Wiley-VCH: Weinheim, 2002.

(36) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822–2827.

(37) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **2000**, *112*, 6532–6542.

(38) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(39) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

(40) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.

(41) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822–8824.

(42) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209–214.

(43) Mclean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639–5648.

(44) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796–6806.

(45) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358–1371.

(46) Frisch, M J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.;

Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.03; Gaussian, Inc.: Wallingford, CT, 2004.

(47) Bader, R. F. *Atoms in Molecules. A Quantum Theory*; Oxford University Press: New York, 1990.

(48) Biegler-König, F.; Schönbohm, J. *AIM2000*, version 2.0; 2002.

(49) Biegler-König, F.; Schönbohm, J.; Bayles, D. *J. Comput. Chem.* **2001**, *22*, 545–559.

(50) Biegler-König, F.; Schönbohm, J. *J. Comput. Chem.* **2002**, *23*, 1489–1494.

(51) Wieser, M. E. *Pure Appl. Chem.* **2006**, *78*, 2051–2066.

(52) Bjellerup, L. *Acta Chem. Scand.* **1961**, *15*, 121–140.

(53) Olofsson, G. Assignment of Uncertainties. In *Experimental Chemical Thermodynamics*; Sunner, S.,Månsson, M., Eds.; Pergamon Press: Oxford, U.K., 1979; Vol. 1, pp 137−159..

(54) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.

(55) Ryskalieva, A. K.; Abramova, G. V.; Erkasov, R. S.; Nurakhmetov, N. N. *Russ. J. Phys. Chem. (Engl. Transl.)* **1992**, *66*, 421–423.

(56) Edwards, J. W.; Kington, G. L. *Trans. Faraday Soc.* **1962**, *58*, 1323–1333.

(57) Andrews, J. T. S.; Westrum, E. F., Jr.; Bjerrum, N. *J. Organomet. Chem.* **1969**, *17*, 293–302.

(58) Atkins, P. W.; de Paula, J. *Physical Chemistry*, 7th ed.; Oxford University Press: Oxford, U.K., 2002; p822.

(59) Pascual-Ahuir, J. L.; Silla, E.; Tunon, I. GEPOL93; http://server.ccl.net/cca/software/SOURCES/FORTRAN/molecular_surface/gepol93/.

(60) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

(61) Denbigh, K. *The Principles of Chemical Equilibrium*, 4th ed.; Cambridge University Press: Cambridge, U.K., 1981.

(62) Irikura, K. K.; Frurip, D. J. *Computational Thermochemistry. Prediction and Estimation of Molecular Thermodynamics*; ACS Symposium Series No. 677; American Chemical Society: Washington, DC, 1998.

(63) Computational Chemistry Comparison and Benchmark DataBase. In *NIST Standard Reference Database 101* (Release 12); National Institute of Standards and Technology: Gaithersburg, MD, 2005.

(64) Aihara, A. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 194–200.

(65) Parsons, G. H.; Rochester, C. H.; Wood, C. E. C. *J. Chem. Soc. B* **1971**, 533–536.

(66) Stull, D. R. *Ind. Eng. Chem.* **1947**, *39*, 517–540.

(67) Bernardes, C. E. S.; Piedade, M. F. M.; Minas da Piedade, M. E. *Cryst. Growth Des.* **2008**, *8*, 2419–2430.

(68) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center: College Station, TX, 1994.

(69) Estácio, S. G.; Cabral do Couto, P.; Costa Cabral, B. J.; Minas da Piedade, M. E.; Martinho Simões, J. A. *J. Phys. Chem. A* **2004**, *108*, 10834–10843.

(70) Scheiner, S. *Hydrogen Bonding. A Theoretical Perspective*; Oxford University Press: New York, 1997.

(71) Pilcher, G.; Sutton, L. E. *J. Chem. Soc.* **1956**, 2695–2700.

(72) DeKruif, C. G.; Smit, E. J.; Govers, H. A. J. *J. Chem. Phys.* **1981**, *74*, 5838–5841.

(73) Bender, R.; Bieling, V.; Maurer, G. *J. Chem. Thermodyn.* **1983**, *15*, 585–594.

(74) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.

(75) Johnson, C. D. *The Hammett Equation*; Cambridge University Press: Cambridge, U.K., 1980.

(76) Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 1–83.

(77) Milton, J. S.; Arnold, J. C. *Probability and Statistics in the Engineering and Computing Sciences*; McGraw-Hill: New York, 1986.

(78) Massart, D. L.; Vandeginste, B. G. M.; Deming, S. N.; Michotte, Y.; Kaufman, L. *Chemometrics: a Textbook*; Elsevier: Amsterdam, 1988.

(79) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255.

(80) Mulder, P.; Korth, D. A.; Pratt, D. A.; DiLabio, G. A.; Valgimigli, L.; Pedulli, G. F.; Ingold, K. U. *J. Phys. Chem. A* **2005**, *109*, 2647–2655.

(81) Angel, L.; Ervin, K. M. *J. Phys. Chem. A* **2006**, *110*, 10392–10403.

(82) Borges dos Santos, R. M.; Costa Cabral, B. J.; Martinho Simões, J. A. *Pure Appl. Chem.* **2007**, *79*, 1369–1382.

JP804455U