10040 *J. Phys. Chem. A* **2008,** *112,* 10040–10045

Molecular Structures of 3-Hydroxybenzoic Acid and 4-Hydroxybenzoic Acid, Obtained by Gas-Phase Electron Diffraction and Theoretical Calculations

Kirsten Aarset,[*,†] **Elizabeth M. Page,**[‡] **and David A. Rice**[‡]

Faculty of Engineering, Oslo University College, P.O. Box 4, St. Olavs Plass, N-0130 Oslo, Norway, and Department of Chemistry, University of Reading, Whiteknights Park, Reading RG6 6AD, U.K.

Received: May 22, 2008; Revised Manuscript Received: July 14, 2008

The structures of 3-hydroxybenzoic acid and 4-hydroxybenzoic acid have been determined by gas-phase electron diffraction using results from quantum chemical calculations to inform the choice of restraints applied to some of the structural parameters. The results from the study presented here demonstrate that resonance hybrids are not as helpful in rationalizing the structures of 2-, 3-, and 4-hydroxybenzoic acids as are models based upon electrostatic effects.

Introduction

Recently, a study was reported of the structures of benzoic acid and 2-hydroxybenzoic acid using results obtained from gas-phase electron diffraction and quantum chemical calculations.[1] In this study evidence was obtained for intramolecular hydrogen bonding between the phenol group and the carbonyl group in the 2- position of gaseous 2-hydroxybenzoic acid.

In a related study of 2-hydroxybenzaldehyde evidence was given for hydrogen bonding between the phenol group and the carbonyl group.[2] The authors describe the hydrogen bond as being resonance assisted. Similar use of a resonance hybrid was invoked to rationalize the hydrogen bond in 2-hydroxybenzoic acid (Figure 1a).[1] The presence of this resonance hybrid was proposed as it would result in a longer C=O distance in 2-hydroxybenzoic acid than that in benzoic acid and a shorter C−C ring distance between the substituents. The observed C−C distances provide positive evidence for the existence of the resonance hybrid; however, the C=O distances do not. To explore the role of the resonance hybrid on the structure of 2-hydroxybenzoic acid, the structures of 3-hydroxy and 4-hydroxybenzoic acids have been determined. Neither of these acids can exhibit intramolecular hydrogen bonds, but 4-hydroxybenzoic acid can possess a resonance hybrid (Figure 1b), which is related to that shown in Figure 1a, while 3-hydroxybenzoic acid cannot. If this resonance hybrid does have an influence on the 4-hydroxybenzoic acid structure, a shorter $C_{ring}-O_{phenolic}$ and a longer C=O bond length compared with those in 3-hydroxybenzoic acid would be expected. The gas-phase structures of 3-hydroxy and 4-hydroxybenzoic acids reported here provide evidence about the role of resonance hybrids upon the gas-phase structures of the three isomers of hydroxybenzoic acid.

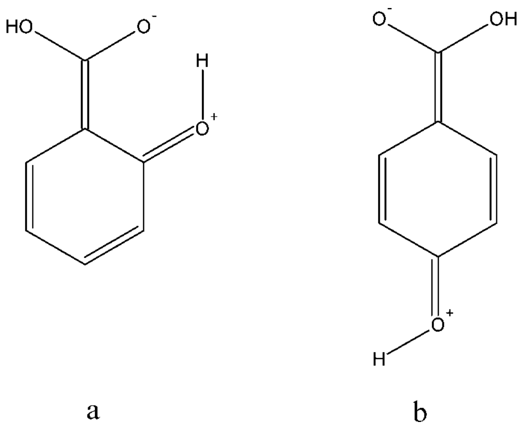

Figure 1. Possible resonance forms for (a) 2-hydroxybenzoic acid and (b) 4-hydroxybenzoic acid.

TABLE 1: Experimental Parameters for 3-Hydroxybenzoic Acid and 4-Hydroxybenzoic Acid

	3-hydroxybenzoic acid		4-hydroxybenzoic acid	
nozzle to plate distance/mm	494.5	244.2	494.8	244.1
nozzle temperature/°C	180	187	190	199
nominal electron wavelength/Å	0.058378	0.058378	0.058378	0.058378
data interval/$Å^{-1}$	0.25	0.25	0.25	0.25
no. of plates	4	3	5	4
$s_{min}/Å^{-1}$	3.0	8.0	3.0	8.0
$s_{max}/Å^{-1}$	14.0	29.0	14.0	29.0
$s_{w1}/Å^{-1}$	5.0	9.0	5.0	9.0
$s_{w2}/Å^{-1}$	12.0	25.0	12.0	25.0
correlation parameter	0.337	0.466	0.38	0.408
scale factor[a]	0.711(9)	0.689(19)	0.709(5)	0.546(17)

[a] Values in parentheses are the estimated standard deviations (1σ).

Experimental Section

Samples of 3-hydroxybenzoic and 4-hydroxybenzoic acid (98% purity) were obtained from the Aldrich Chemical Co. and used without further purification. Electron diffraction data were obtained at two different camera distances with an accelerating voltage of 42 kV using the apparatus at the University of Reading. Scattering intensities were recorded on digital image plates and measured using a Fuji BAS1800II Image Plate system. The electron wavelength was determined by calibration with benzene vapor. Experimental parameters, namely temperatures, nozzle-to-plate distances, weighting functions for creating weight matrices, correlation parameters, final scaling factors, and electron wavelengths for both compounds are listed in Table 1. Data reduction was performed using standard routines[3] employing published scattering factors.[4] Data analysis was carried out using the program "ed@ed".[5] The experimental

---

[†] Oslo University College.

[‡] University of Reading.

10.1021/jp804539u CCC: $40.75

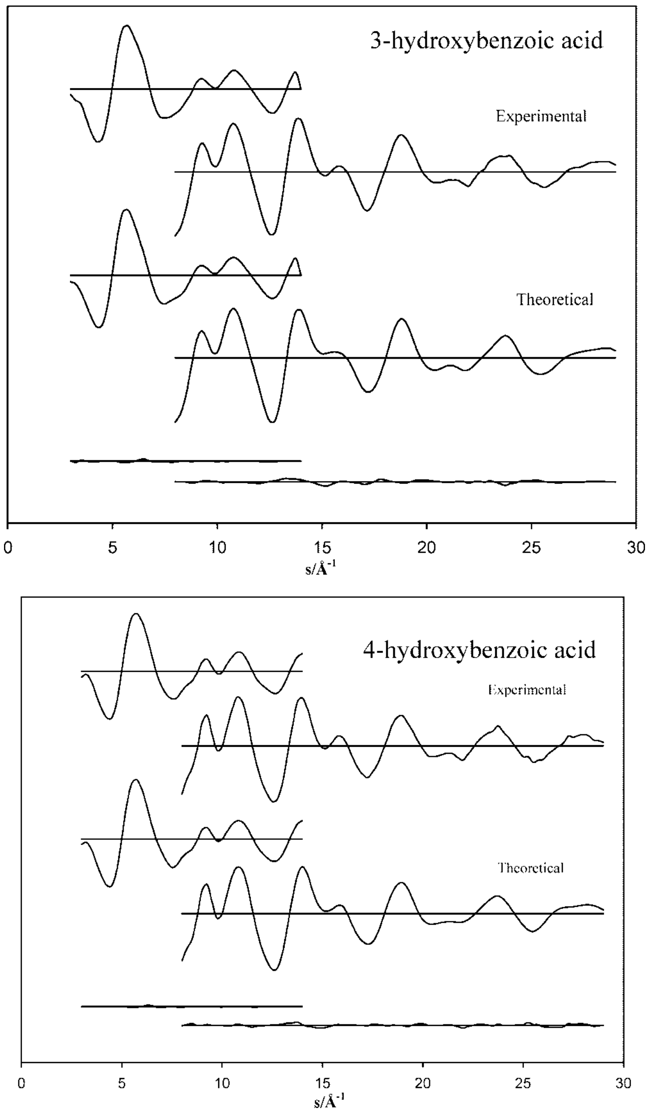

Figure 2. Average experimental and theoretical intensity curves, $s^4I_t(s)$, for 3-hydroxybenzoic acid and 4-hydroxybenzoic acid.

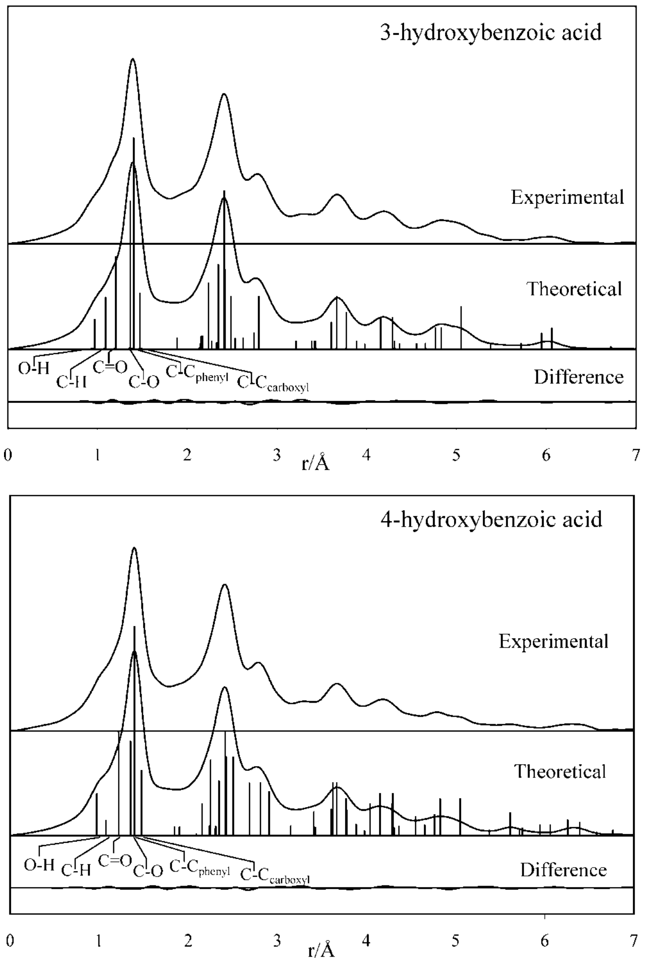

Figure 3. Radial distribution curves for 3-hydroxybenzoic acid and 4-hydroxybenzoic acid. The difference curve is experimental minus theoretical. The vertical lines indicate important interatomic distances and have lengths proportional to the distance weights. Before Fourier inversion, the data were multiplied by $s\cdot\exp(-0.00002s^2)/(Z_C - f_C)(Z_O - f_O)$.

intensity curves are shown in Figure 2. Radial distribution (RD) curves are presented in Figure 3.

Theoretical Calculations

Molecular Orbital Calculations. Ab initio molecular orbital calculations at Hartree−Fock (HF) and second-order Møller−Plesset (MP2) level of theory with the 6−311+G(d,p) basis set, using the Gaussian98 program,[6] indicated that 3-hydroxybenzoic acid exists as a mixture of eight stable conformers and 4-hydroxybenzoic acid as a mixture of four stable conformers. The important geometrical parameters obtained from the theoretical calculations for the low-energy forms are shown in Table 2, and the energy differences are given in Table 3. The restraints used for some of the structural parameters in the electron diffraction model described below were obtained from the difference between the MP2/6−311+G(d,p) and the HF/6−311+G(d,p) calculations. Values from MP2/6−311+G(d,p) calculations were used to constrain the CCH_{ring} angle and torsional angles.

Normal Coordinate Calculations. Vibrational data play an important part in the refinement of any model used to analyze the experimental gas-phase electron diffraction data. Ab initio frequency calculations (HF/6-311+G(d,p)) provided theoretical force fields for the molecular vibrations. To calculate the required vibrational parameters (amplitudes, perpendicular corrections, and centrifugal distortions) from these force fields the program SHRINK[7,8] was used. The force constants for the distances were scaled by 0.9. The calculated vibrational data were needed to convert the r_a distances obtained from the electron diffraction model to obtain a set of geometrically consistent distances (r_{h1}).

Analysis of the Gas-Phase Electron Diffraction Data. ***3-Hydroxybenzoic Acid.*** As stated earlier, theoretical calculations, using Hartree−Fock and Møller−Plesset level of theory, gave evidence for eight stable conformers for 3-hydroxybenzoic acid. Four of these conformers are approximately 30 kJ mol^{-1} lower in energy than the others, and only these were included in the theoretical model used in the analysis of the electron diffraction data. The common feature of these four low-energy forms not shared by the four high-energy forms is the coplanarity of the phenyl ring and the carboxyl group and the eclipsing of the $O-H_{carboxyl}$ and C═O bonds. In all the high-energy conformers, the carboxyl group is 20−30° out of the plane of the phenyl ring and the $O-H_{carboxyl}$ and C═O bonds are *anti* to each other. Two of the low-energy conformers have the C═O directed toward the $O-H_{phenyl}$ (**1** and **2** in Figure 4), and the other two have the $O-H_{carboxyl}$ (**3** and **4** in Figure 4) directed toward the $O-H_{phenyl}$.

TABLE 2: Results from the ab Initio Calculations (6-311+G(d,p)) for the Low-Energy Forms (Conformer 1)[a] of 3-Hydroxybenzoic Acid and 4-Hydroxybenzoic Acid

	3-hydroxybenzoic acid		4-hydroxybenzoic acid	
parameter[b]	HF	MP2	HF	MP2
$r(O_{8/9}-H_{16})$	0.941	0.963	0.941	0.963
$r(O_{14}-H_{15})$	0.946	0.968	0.946	0.968
$r(C-H)_{ave}$	1.074	1.086	1.142	1.156
$r(C=O)$	1.185	1.214	1.187	1.214
$r(C_{12}-O_{14})$	1.327	1.357	1.330	1.359
$r(C_{3/4}-O_{8/9})$	1.350	1.366	1.343	1.366
$r(C_1-C_2)$	1.391	1.403	1.393	1.405
$r(C_2-C_3)$	1.380	1.397	1.378	1.394
$r(C_3-C_4)$	1.389	1.402	1.389	1.401
$r(C_4-C_5)$	1.380	1.397	1.389	1.401
$r(C_5-C_6)$	1.388	1.400	1.381	1.395
$r(C_1-C_6)$	1.384	1.402	1.388	1.402
$r(C_{phenyl}-C_{12})$	1.491	1.488	1.481	1.485
$\angle C_1C_2C_3$	119.7	119.6	120.7	120.2
$\angle C_2C_3C_4$	120.0	120.2	119.6	120.0
$\angle C_3C_4C_5$	119.8	119.6	120.3	120.1
$\angle C_4C_5C_6$	120.8	120.9	119.6	119.9
$\angle C_5C_6C_1$	118.9	118.9	120.7	120.2
$\angle C_2C_1C_6$	120.7	120.7	119.1	119.7
$\angle C_2C_1C_{12}$	117.4	117.0	122.4	122.3
$\angle C_6C_1C_{12}$	121.9	122.2	118.5	118.0
$\angle C_{2/3}C_{3/4}O_{8/9}$	122.6	122.7	117.4	117.1
$\angle C_{4/5}C_{3/4}O_{8/9}$	117.4	117.0	122.3	122.8
$\angle CCH_{phenyl,ave}$	119.9	120.0	120.0	120.0
$\angle C_{3/4}O_{8/9}H_{16}$	111.2	108.6	111.4	108.7
$\angle C_1C_{12}O_{13}$	124.4	124.7	124.7	124.9
$\angle C_1C_{12}O_{14}$	113.5	112.7	113.5	112.6
$\angle O_{13}C_{12}O_{14}$	122.1	122.6	121.8	122.4
$\angle C_{12}O_{14}H_{15}$	108.4	105.6	108.3	105.5
$\Phi C_2C_1C_{12}O_{13}$	0	0	−180	−180
$\Phi C_2C_1C_{12}O_{14}$	−180	−180	0	0
$\Phi C_6C_1C_{12}O_{13}$	−180	−180	0	0
$\Phi C_6C_1C_{12}O_{14}$	0	0	−180	−180
$\Phi C_{2/3}C_{3/4}O_{8/9}H_{16}$	0	0	0	0
$\Phi C_{4/5}C_{3/4}O_{8/9}H_{16}$	180	180	180	180
$\Phi O_{13}C_{12}O_{14}H_{15}$	0	0	0	0

[a] The two low-energy conformers are depicted in Figures 4 and 5. [b] Distances are in angstrøm (Å), and angles are in degree (deg).

TABLE 3: Energy Differences for the Conformers of 3-Hydroxybenzoic Acid and 4-Hydroxybenzoic Acid Obtained by ab Initio Calculations (6-311+G(d,p))

	3-hydroxybenzoic acid		4-hydroxybenzoic acid	
conformers[a]	HF, kJ/mol	MP2[b], kJ/mol	HF, kJ/mol	MP2, kJ/mol
1	0.0	0.0	0.0	0.0
2	3.2	2.9	0.3	0.2
3	1.6	1.2	36.3	26.5
4	2.7	2.7	35.3	*c*
5	31.6			
6	35.3			
7	36.7			
8	34.2			

[a] The low-energy conformers are depicted in Figures 4 and 5. [b] MP2 calculations were only performed for the four low-energy forms. [c] Not calculated.

In the theoretical model used in the electron diffraction analysis, the four low-energy conformers were treated as two groups. Each group contains two conformers where the only difference between them is the direction of the OH_{phenyl} vector (group 1 consists of conformers **1** and **2** and group 2 of conformers **3** and **4**; see Figure 4). The structural parameters for the conformers in each group were assumed to be equal.

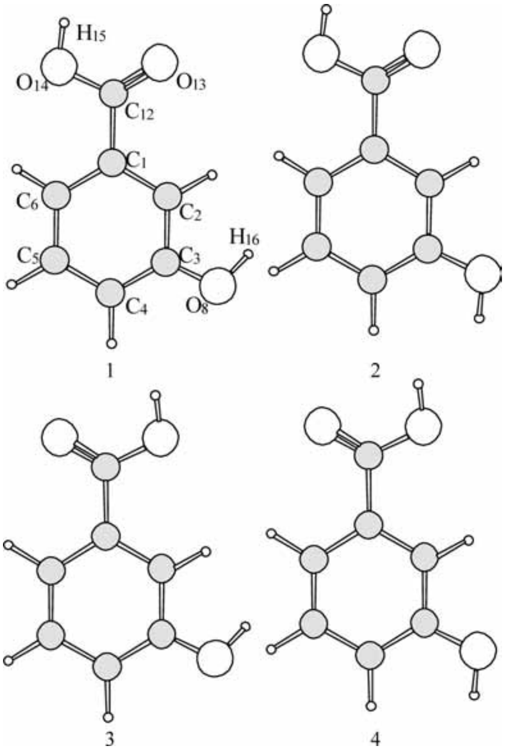

Figure 4. Diagram showing the four low-energy conformers of 3-hydroxybenzoic acid and the numbering scheme.

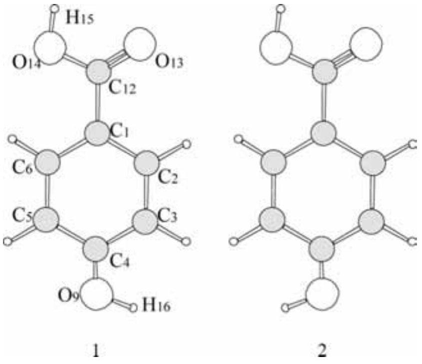

Figure 5. Diagram showing the two low-energy conformers of 4-hydroxybenzoic acid and the numbering scheme.

The energy differences between all the conformers are given in Table 3, and the four low-energy conformers are depicted in Figure 4.

4-Hydroxybenzoic Acid. Theoretical calculations, using Hartree−Fock level of theory, gave evidence for four stable conformers for 4-hydroxybenzoic acid, two of which were at markedly lower energy than the others (approximately 35 kJ mol^{-1}). These forms, as was found with the low-energy conformers of 3-hydroxybenzoic acid, have the carboxyl group coplanar with the phenyl ring and the O−H group eclipsing the C=O bond of the carboxyl group, and only these conformers were included in the theoretical model used in the analysis of the electron diffraction data. Both high-energy conformers have the carboxyl group 20−30° out of the plane, and the $O-H_{carboxyl}$ and C=O bonds are *anti* to each other. In the theoretical model the two low-energy conformers were treated as one group since the only difference between them is the direction of the OH_{phenyl} vector. The structural parameters for the conformers were assumed to be equal. The energy differences between all the conformers are given in Table 3, and the two low-energy conformers are depicted in Figure 5.

TABLE 4: Structural Parameters Obtained from Electron Diffraction (GED) Refinements and Theoretical Calculations (MP2/6-311+G(d,p)) for the Low-Energy Forms of 3-Hydroxybenzoic Acid and 4-Hydroxybenzoic Acid

	3-hydroxybenzoic acid			4-hydroxybenzoic acid		
	GED		ab initio	GED		ab initio
independent parameters[a]	$r_{h1}/\angle_{h1}$	restraint	$r_e/\angle_e$	$r_{h1}/\angle_{h1}$	restraint	$r_e/\angle_e$
$r(C_1-C_2)$	1.405(3)		1.403	1.406(3)		1.405
$r(C_1-C_2) - r(C_2-C_3)$	0.007(4)	0.004	0.006	0.012(3)	0.004	0.011
$r(C_1-C_2) - r(C_3-C_4)$	−0.001(0)	0.001	−0.001	0.004(0)	0.001	0.004
$r(C_1-C_2) - r(C_4-C_5)$	0.006(5)	0.005	0.006	0.003(1)	0.001	0.003
$r(C_1-C_2) - r(C_5-C_6)$	0.003(1)	0.001	0.004	0.009(2)	0.002	0.010
$r(C_1-C_2) - r(C_1-C_6)$	0.000(6)	0.006	0.001	0.003(1)	0.002	0.003
$r(C_1-C_2) - r(C_1-C_{12})$	−0.060(9)	0.015	−0.085	−0.071(6)	0.007	−0.081
$r(C_{phenyl}-H)$	1.104(12)		1.086	1.074(8)	0.012	1.086
$r(C{=}O)$	1.200(5)		1.213	1.208(6)		1.214
$\frac{1}{2}[r(C_{12}-O_{14}) + r(C_2-O_7)]$	1.362(7)		1.362	1.365(8)		1.363
$r(C_2-O_7) - r(C_{12}-O_{14})$	−0.008(3)	0.003	−0.010	−0.004(5)	0.006	−0.007
$\frac{1}{2}[r(O_{8/9}-H_{16}) + r(O_{14}-H_{15})]$	0.959(15)		0.966	0.975(14)	0.009	0.966
$r(O_{8/9}-H_{16}) - r(O_{14}-H_{15})$	−0.005(1)	0.001	−0.005	−0.005(1)	0.001	−0.005
$\frac{1}{2}(\angle C_2C_1C_6 + \angle C_1C_2C_3)$	119.8(1)		120.2	119.9(1)		119.9
$\angle C_2C_1C_6 - \angle C_1C_2C_3$	1.2(2)	0.2	1.2	0.2(7)	1.7	−0.5
$\angle C_1C_2C_3 - \angle C_1C_6C_5$	0.1(1)	0.1	0.1	0.0(1)	0.1	0.0
$\angle C_6C_1C_{12}$	119.1(9)		122.2	121.4(20)		118.0
$\angle C_1C_{12}O_{13}$	124.1(9)		124.7	126.0(21)		125.0
$\angle C_1C_{12}O_{14}$	114.1(10)		112.7	111.0(20)		112.6
$\angle C_{2/3}C_{3/4}O_{8/9}$	122.0(15)		122.8	117.6(19)		117.1
$\angle CCH_{phenyl,ave}$	120.0		120.0	120.0		120.0
$\angle C_{3/4}O_{8/9}H_{16}$	108.2(23)	2.6	108.6	110.0(23)	0.4	108.7
$\angle C_{12}O_{14}H_{15}$	107.7(26)	2.8	105.6	105.1(25)	1.3	105.5
$\Phi C_2C_1C_{12}O_{13}$	0		0	0		0
$\Phi O_{13}C_{12}O_{14}H_{15}$	0		0	0		0
$\Phi CCO_{8/9}H$	0		0	0		0
α[b]	79(2)		63			
distances/angles[a]	$r_a/\angle_{h1}$	l_{exp}	l_{theo}	$r_a/\angle_{h1}$	l_{exp}	l_{theo}
$r(O_{8/9}-H_{16})$	0.959(15)	0.066	0.066	0.975(14)	0.065	0.065
$r(O_{14}-H_{15})$	0.954(15)	0.066	0.066	0.970(14)	0.066	0.066
$r(C-H)_{phenyl}$	1.100(12)	0.074	0.074	1.071(8)	0.073	0.073
$r(C{=}O)$	1.200(5)	0.032(18)	0.036	1.208(6)	0.026(15)	0.036
$r(C_{3/4}-O_{8/9})$	1.365(7)	0.044	0.044	1.365(8)	0.065	0.044
$r(O_{14}-C_{12})$	1.357(7)	0.044	0.044	1.362(8)	0.065	0.044
$r(C_1-C_2)$	1.403(3)	0.052(4)	0.046	1.405(3)	0.049(6)	0.046
$r(C_2-C_3)$	1.396(4)	0.052(4)	0.045	1.393(4)	0.049(6)	0.045
$r(C_3-C_4)$	1.404(3)	0.052(4)	0.046	1.401(3)	0.049(6)	0.045
$r(C_4-C_5)$	1.397(5)	0.052(4)	0.045	1.402(3)	0.049(6)	0.046
$r(C_5-C_6)$	1.399(3)	0.052(4)	0.046	1.395(3)	0.049(6)	0.045
$r(C_1-C_6)$	1.403(5)	0.052(4)	0.045	1.402(3)	0.049(6)	0.045
$r(C_1-C_{12})$	1.463(8)	0.049(2)	0.049	1.476(6)	0.048	0.048
$r(C_1\cdots O_{13})$	2.357(13)		0.059	2.398(23)	0.058	
$r(C_1\cdots O_{14})$	2.368(16)		0.064	2.342(26)	0.063	
$r(O_{8/9}\cdots O_{13})$	5.093(26)		0.132	6.431(14)	0.095	
$r(O_{8/9}\cdots O_{14})$	6.036(10)		0.083	6.314(16)	0.102	
$r(C_2\cdots O_{13})$	2.846(16)		0.101	2.890(12)	0.065	
$r(C_6\cdots O_{14})$	2.680(20)		0.105	2.715(11)	0.069	
$r(C_6\cdots O_{13})$	3.609(15)		0.066	3.633(31)	0.101	
$r(C_2\cdots O_{14})$	3.690(16)		0.070	3.625(33)	0.104	
$\angle C_1C_2C_3$	119.2(1)			119.8(1)		
$\angle C_2C_3C_4$	121.5(1)			120.4(1)		
$\angle C_3C_4C_5$	118.2(1)			119.7(1)		
$\angle C_4C_5C_6$	121.6(1)			120.3(1)		
$\angle C_1C_6C_5$	119.2(1)			119.8(1)		
$\angle C_2C_1C_6$	120.4(1)			120.0(1)		

[a] Distances are in angstrøm (Å), and angles are in degree (deg). Uncertainties are given as 1σ. [b] The amount of conformer group 1 (conformer **1** and **2** in Figure 4).

The structures of 3-hydroxybenzoic and 4-hydroxybenzoic acid were defined in terms of 27 and 26 independent geometrical parameters, respectively (see Table 4). In the models employed all the C−H distances and CCH angles were assumed to be equal for each molecule. Flexible restraints were used during refinements by use of the SARACEN method.[9,10] Of the independent parameters, 11 and 8 were unrestrained in the refinements of the data for 3-hydroxybenzoic acid and 4-hydroxybenzoic acid, respectively (see Table 4). Values for the dependent parameters from the final refinements are given in Table 4. Intensity curves calculated for the final models are shown in Figure 2, together with experimental and difference

TABLE 5: Correlation Matrixes for 3-Hydroxybenzoic Acid and 4-Hydroxybenzoic Acid[a]

3-Hydroxybenzoic Acid

		1	2	3	4	5	6	7	8	9	10	11	12
1	$r(C_1-C_2)$	100	61		−62					−53			
2	$r(C_1-C_2) - r(C_1-C_{12})$		100										
3	$r(C{=}O)$			100		51							
4	$^1/_2[r(C_{12}-O_{14}) + r(C_2-O_7)]$				100					71			
5	$^1/_2[r(O_{8/9}-H_{16}) + r(O_{14}-H_{15})]$					100							
6	$r(C_{phenyl}-H)$						100						54
7	$\angle C_1C_{12}O_{13}$							100	−73		58		
8	$\angle C_1C_{12}O_{14}$								100	57	−62		
9	$\angle C_2C_3O_8$									100			
10	$\angle C_6C_1C_{12}$										100		
11	$l(C_1-C_{12})$											100	−55
12	$l(C{=}O)$												100

4-Hydroxybenzoic Acid

		1	2	3	4	5	6
1	$r(C_1-C_2)$	100	−83				
2	$^1/_2[r(C_{12}-O_{14}) + r(C_2-O_7)]$		100				58
3	$\angle C_1C_{12}O_{13}$			100	−90	95	
4	$\angle C_1C_{12}O_{14}$				100	−96	
5	$\angle C_6C_1C_{12}$					100	
6	$l(C_1-C_2)$						100

[a] Only correlation factors larger than 50 are shown.

TABLE 6: Comparison of r_a Values for Benzoic Acid and 2-, 3-, and 4-Hydroxybenzoic Acid

parameters[a]	3-hydroxybenzoic acid	4-hydroxybenzoic acid	2-hydroxybenzoic acid	benzoic acid
$r(C_{ring}-C_{carboxyl})$	1.463(8)	1.476(6)	1.465(8)	1.484(6)
$r(C{=}O)$	1.200(5)	1.208(6)	1.228(6)	1.225(6)
$r(C_{carboxyl}-OH)$	1.357(7)	1.362(8)	1.339(7)	1.367(8)
$r(C_{ring}-O_{phenolic})$	1.365(7)	1.365(8)	1.333(7)	
$\angle C_6C_1C_{12}$	119.1(9)	121.3(20)	119.0(12)	124.0(11)
$\angle C_1C_{12}O_{13}$	124.1(9)	126.0(21)	122.6(9)	126.6(16)
$\angle C_1C_{12}O_{14}$	114.1(10)	111.1(20)	116.2(11)	113.1(15)
$\angle O_{13}C_{12}O_{14}$	121.8(11)	122.9(21)	121.2(11)	120.3(15)
reference	this work	this work	1	1

[a] Distances (r_a) are in angstrøm (Å), and angles are in degree (deg). Uncertainties are given as 1σ.

curves. Figure 3 contains the corresponding RD-curves, and the correlation matrixes for the refined parameters are given in Table 5.

Results and Discussion

Gaseous 3-hydroxybenzoic acid and 4-hydroxybenzoic acid were found to be in the low-energy forms in which the carboxyl group is coplanar with the phenyl ring. The bond lengths (r_a), bond angles, and torsions obtained for both species obtained from the electron diffraction analysis are listed in Table 4. One of the motivations for the present study was to search for evidence for the influence of the resonance hybrid shown in Figure 1b on the structure of 4-hydroxybenzoic acid by examining the variation in the $C_{ring}-O_{phenolic}$, $C{=}O$, $C_{carboxyl}-OH$, $C_{ring}-C_{carboxyl}$ distances with the position of the OH group in the phenyl ring. The data are presented in Table 6 where it can be seen that the $r(C_{ring}-C_{carboxyl})$, $r(C{=}O)$, $r(C_{carboxyl}-OH)$, and $r(C_{ring}-O_{pehnolic})$ distances shown by 4-hydroxybenzoic acid show no significant differences from the comparable distances in 3-hydroxybenzoic acid. Thus there is clearly no evidence for the resonance hybrid shown in Figure 1b having an influence upon the structure of 4-hydroxybenzoic acid.

It is questionable whether the resonance hybrid shown in Figure 1a has any influence upon the structure of 2-hydroxybenzoic acid as has been suggested.[1] The $C_{ring}-C_{carboxyl}$ distance of 2-hydroxybenzoic acid (1.465(8) Å) is similar to those of the other two isomers (see Table 6), and if the structure shown in Figure 1a were influential, a shorter distance should be observed, but this is not the case. The resonance hybrid shown in Figure 1a for 2-hydroxybenzoic acid does explain the observed $C{=}O$ bond length but fails to explain the shorter $C_{carboxyl}-OH$ distance (see Table 6). An alternative explanation for the structural differences is provided by a consideration of the electrostatic influence of the intramolecular hydrogen bond in 2-hydroxybenzoic acid.

The presence of an internal hydrogen bond in 2-hydroxybenzoic acid would lead to a decrease in the electron density on the carbonyl oxygen atom and so, a priori, a longer $C{=}O$ bond in gaseous 2-hydroxybenzoic acid than in benzoic acid, 3-hydroxybenzoic acid, and 4-hydroxybenzoic acid, and indeed this is observed (see Table 6). Such a bond lengthening results in an increase in electrophilicity of the carbon atom of the carboxyl group in 2-hydroxybenzoic acid which would lead to a decrease in the $C_{carboxyl}-OH$ bond length as is also observed. The intramolecular hydrogen bond in 2-hydroxybenzoic acid would lead to an increase in length of the O−H bond in the phenolic group and hence an increase in electron density on the phenolic oxygen atom and, as a result, a shorter $C_{ring}-O_{phenolic}$ distance compared with the equivalent ones in 3-and 4-hydroxybenzoic acids. The shortening is quite pronounced (≈0.032 Å) as can be seen from Table 6.

The arguments above and the related structural data provide strong evidence for hydrogen bonding in gaseous 2-hydroxybenzoic acid, and this can be rationalized by considering electrostatic or inductive effects. The similarity between the structural data of 3- and 4-hydroxybenzoic acids presented in this paper weakens the argument for the case of resonance hybrids as discussed previously.[1] In fact, the approach invoked in this work could be applied equally well to related systems such as 2-hydroxybenzaldehyde.[2]

Acknowledgment. This work has received support from The Research Council of Norway (Program for Supercomputing) through a grant of computing time. We thank Professor David W. H. Rankin of the University of Edinburgh for allowing us to use his suite of programs (see refs 5, 9, and 10). We also thank Mr. Alan Adams from the University of Reading for technical assistance and expertise.

References and Notes

(1) Aarset, K.; Page, E. M.; Rice, D. A. *J. Phys. Chem. A* **2006**, *110*, 9014.

(2) Borisenko, K. B.; Bock, C. W.; Hargittai, I. *J. Phys. Chem.* **1996**, *100*, 7426.

(3) Hagen, K.; Hobson, R. J.; Howill, C. J.; Rice, D. A. *Inorg. Chem.* **1986**, *25*, 3659.

(4) Ross, A. W.; Fink, M.; Hilderbrandt, R. *Int. Tables of X-Ray Crystallography, Vol. C, 245*; Kluwer Academic Publishers: Dordrecht, Boston, and London, 1992.

(5) Hinchley, S. L.; Robertson, H. E.; Borisenko, K. B.; Turner, A. R.; Johnston, B. F.; Rankin, D. W. R.; Ahmadian, M.; Jones, J. N.; Cowley, A. H. *Dalton Trans.* **2004**, 2469.

(6) Gaussian 98, Revision A.11, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K., Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; 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.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc.: Pittsburgh PA, 2001.

(7) Sipachev, V. A. *J. Mol. Struct.* **2001**, *567*, 67.

(8) Sipachev, V. A. *J. Mol. Struct.* **1985**, *121*, 143.

(9) Blake, A. J.; Brain, T. P.; McNab, H.; Miller, J.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H.; Robertson, H. E.; Smart, B. A. *J. Phys. Chem.* **1996**, *100*, 12280.

(10) Brain, P. T.; Morrison, C. A.; Parson, S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1996**, 4589.

JP804539U