Molecular Structures of Benzoic Acid and 2-Hydroxybenzoic Acid, Obtained by Gas-Phase Electron Diffraction and Theoretical Calculations

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

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

Received: April 4, 2006; In Final Form: May 3, 2006

The structures of benzoic acid (C_6H_5COOH) and 2-hydroxybenzoic acid ($C_6H_4OHCOOH$) have been determined in the gas phase by electron diffraction using results from quantum chemical calculations to inform restraints used on the structural parameters. Theoretical methods (HF and MP2/6-311+G(d,p)) predict two conformers for benzoic acid, one which is 25.0 kJ mol^{-1} (MP2) lower in energy than the other. In the low-energy form, the carboxyl group is coplanar with the phenyl ring and the O−H group eclipses the C═O bond. Theoretical calculations (HF and MP2/6-311+G(d,p)) carried out for 2-hydroxybenzoic acid gave evidence for seven stable conformers but one low-energy form (11.7 kJ mol^{-1} lower in energy (MP2)) which again has the carboxyl group coplanar with the phenyl ring, the O−H of the carboxyl group eclipsing the C═O bond and the C═O of the carboxyl group oriented toward the O−H group of the phenyl ring. The effects of internal hydrogen bonding in 2-hydroxybenzoic acid can be clearly observed by comparison of pertinent structural parameters between the two compounds. These differences for 2-hydroxybenzoic acid include a shorter exocyclic C−C bond, a lengthening of the ring C−C bond between the substituents, and a shortening of the carboxylic single C−O bond.

Introduction

Gas-phase electron diffraction studies on substituted phenols such as 2-hydroxybenzaldehyde[1] (salicylaldehyde) and nitrophenol[2−4] have demonstrated the existence of intramolecular hydrogen bonding which manifests itself in significant structural changes in certain bond lengths and angles in the molecules as compared to the respective unsubstituted compounds. For nitrophenol the comparable molecules are phenol and nitrobenzene, while for 2-hydroxybenzaldehyde the comparators are phenol and benzaldehyde. The structural results for benzoic acid and 2-hydroxybenzoic acid were consistent with those obtained from molecular orbital calculations and were interpreted in terms of resonance-assisted hydrogen bonding.[5] The effects of intramolecular hydrogen bonding are translated to the solid state and were also observed in X-ray crystallographic investigations carried out on 2-nitrophenol[6] and 2-hydroxybenzaldehyde. The latter has been the subject of a low-temperature X-ray study[7] and has also been investigated as the 2-hydroxybenzaldehyde−gossypol complex.[8] Structural evidence from these two substituted phenol systems suggests that internal hydrogen bonding is likely to be a feature in similar molecules. We therefore decided to embark upon a study of benzoic acid and its phenolic derivative, 2-hydroxybenzoic acid (salicylic acid). In this paper we report the gas-phase structures of both molecules (C_6H_5COOH and $C_6H_4OHCOOH$) as studied by electron diffraction and quantum chemical calculations. We present strong evidence to support the presence of intramolecular hydrogen bonding within the substituted molecule 2-hydroxybenzoic acid.

TABLE 1: Experimental Parameters for Benzoic Acid (C_6H_5COOH) and 2-Hydroxybenzoic Acid ($C_6H_4OHCOOH$)

	benzoic acid		2-hydroxybenzoic acid	
nozzle-to-plate distance/mm	494.4	243.9	494.5	244
nozzle temperature/°C	130	135	138	147
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	5	3	3
s_{min}/Å^{-1}	3	8	3	8
s_{max}/Å^{-1}	14	29	14	29
s_{w1}/Å^{-1}	5	10	5	10
s_{w2}/Å^{-1}	12	25	12	25
correlation parameter	0.442	0.4785	0.3945	0.3174
scale factor[a]	0.515(7)	0.784(28)	0.640(4)	0.756(16)

[a] Values in parentheses are the estimated standard deviations.

Experimental Section

Gas-Phase Electron Diffraction Data Collection. Samples of benzoic acid and 2-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 off-diagonal 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[9] employing published scattering factors.[10] Data analysis was carried out using the program "ed@ed".[11] The experimental

---

* Corresponding author. E-mail: kirsten.aarset@iu.hio.no.
† Oslo University College.
‡ University of Reading.

10.1021/jp0620825 CCC: $33.50

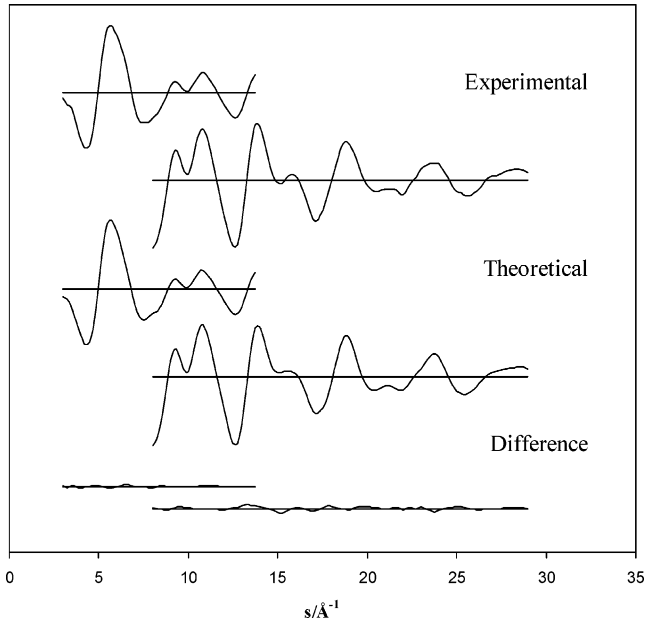

Figure 1. Average experimental and theoretical intensity curves, $s^4I_t(s)$, for benzoic acid.

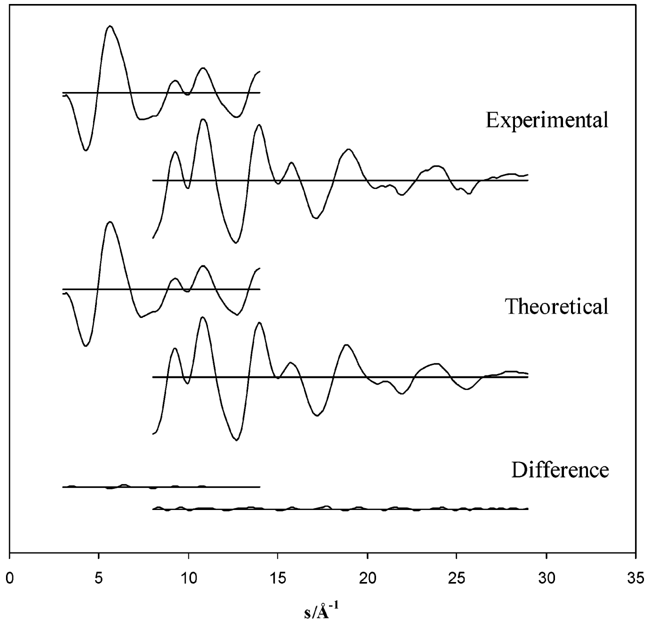

Figure 2. Average experimental and theoretical intensity curves, $s^4I_t(s)$, for 2-hydroxybenzoic acid.

intensity curves are shown in Figures 1 and 2, respectively, for benzoic acid and 2-hydroxybenzoic acid. Radial distribution (RD) curves for the final models of the molecules are presented in Figures 3 and 4 for benzoic acid and 2-hydroxybenzoic acid, respectively.

Theoretical Calculations

Molecular Orbital Calculations. Ab-initio molecular orbital calculations at the 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,[12] indicated that benzoic acid exists as a mixture of two stable conformers and 2-hydroxybenzoic acid as a mixture of seven stable conformers. Some of the geometrical parameters obtained from the theoretical calculations are shown in Table 2. 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_{phenyl} angle and torsional angles.

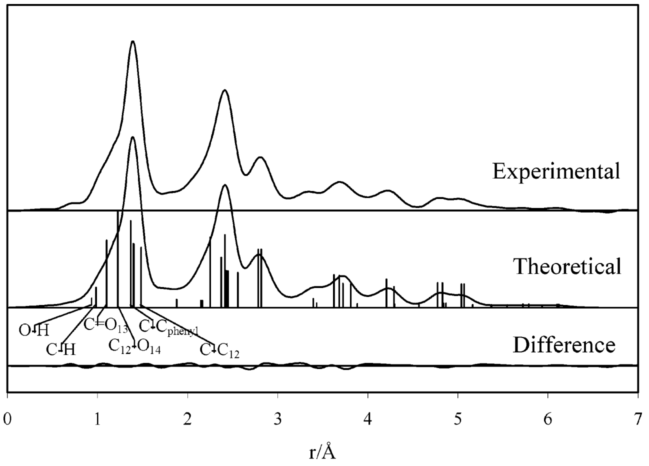

Figure 3. Radial distribution curves for benzoic acid. Difference curve is experimental minus theoretical. The vertical lines indicate important interatomic distances and have lengths proportional to the distance weights. Before Fourier inversion the data were multiplied by $s\cdot\exp(-0.00002s^2)/(Z_C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

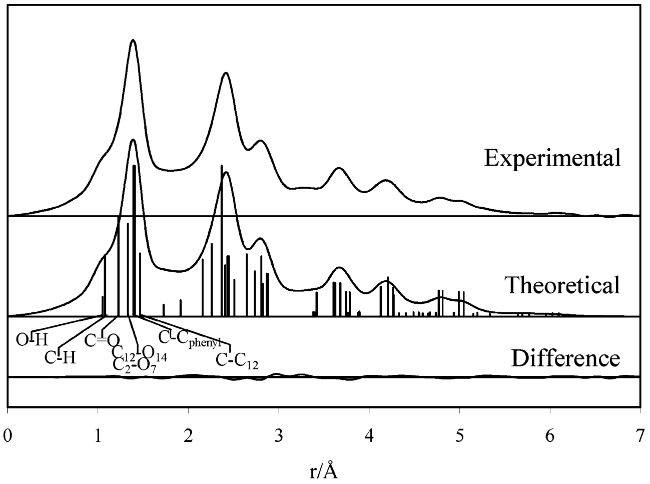

Figure 4. Radial distribution curves for 2-hydroxybenzoic acid. Difference curve is experimental minus theoretical. The vertical lines indicate important interatomic distances and have lengths proportional to the distance weights. Before Fourier inversion the data were multiplied by $s\cdot\exp(-0.00002s^2)/(Z_C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

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 ASYM40[13] 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_α).

Analysis of the Gas-Phase Electron Diffraction Data. *Benzoic Acid.* As stated earlier, theoretical calculations, using the Hartree−Fock and Møller−Plesset level of theory, gave evidence for two stable conformers for benzoic acid. One is a low-energy form with the carboxyl group coplanar with the

TABLE 2: Results from Ab-Initio Calculations for the Low-Energy Form of Benzoic Acid and 2-Hydroxybenzoic Acid

	benzoic acid		2-hydroxybenzoic acid	
parameter[a]	HF/6-311+G(d,p)	MP2/6-311+G(d,p)	HF/6-311+G(d,p)	MP2/6-311+G(d,p)
$r(O_{14}-H_{15})$	0.946	0.968	0.946	0.969
$r(O_7-H_{16})$			0.949	0.977
$r(C-H)_{ave}$	1.074	1.086	1.074	1.086
$r(C_{12}=O_{13})$	1.185	1.213	1.197	1.227
$r(C_{12}-O_{14})$	1.329	1.358	1.322	1.348
$r(C_2-O_7)$			1.328	1.349
$r(C_5-C_6)$	1.385	1.398	1.372	1.391
$r(C_3-C_4)$	1.387	1.401	1.373	1.392
$r(C_2-C_3)$	1.383	1.397	1.396	1.405
$r(C_4-C_5)$	1.386	1.400	1.396	1.405
$r(C_1-C_2)$	1.390	1.403	1.400	1.415
$r(C_1-C_6)$	1.389	1.404	1.401	1.410
$r(C_{phenyl}-C_{12})$	1.488	1.490	1.472	1.473
$\angle C_2C_1C_6$	120.0	120.3	119.3	119.8
$\angle C_1C_2C_3$	120.0	119.7	119.3	119.1
$\angle C_2C_3C_4$	119.9	120.2	120.2	120.5
$\angle C_3C_4C_5$	120.3	119.9	121.1	120.6
$\angle C_4C_5C_6$	120.0	120.3	118.9	119.6
$\angle C_1C_6C_5$	119.9	119.5	121.2	120.5
$\angle C_2C_1C_{12}$	118.1	117.7	119.7	118.8
$\angle C_6C_1C_{12}$	121.9	121.9	121.0	121.3
$\angle C_1C_2O_7$			123.8	123.5
$\angle C_3C_2O_7$			116.9	117.4
$\angle CCH_{phenyl,\ ave}$	120.0	120.0	119.8	119.9
$\angle C_2O_7H_{16}$			110.6	106.8
$\angle C_1C_{12}O_{13}$	124.6	124.8	124.5	124.4
$\angle C_1C_{12}O_{14}$	113.5	112.6	114.5	114.1
$\angle O_{13}C_{12}O_{14}$	122.0	122.5	121.0	121.5
$\angle C_{12}O_{14}H_{15}$	108.3	105.5	108.4	105.8
$\Phi C_2C_1C_{12}O_{13}$	0	0	0.0	0.3
$\Phi C_2C_1C_{12}O_{14}$	180	180	180.0	179.7
$\Phi C_6C_1C_{12}O_{13}$	180	180	180.0	179.8
$\Phi C_6C_1C_{12}O_{14}$	0	0	0.0	0.2
$\Phi C_1C_2O_7H_{16}$			0.0	0.0
$\Phi C_3C_2O_7H_{16}$			180.0	179.9
$\Phi O_{13}C_{12}O_{14}H_{15}$	0	0	0.0	0.1

[a] Distances are in angstrøms (Å), and angles are in degrees (°).

TABLE 3: Energy Differences for the Conformers of Benzoic Acid and 2-Hydroxybenzoic Acid Obtained by Ab-Initio (HF/6-311+G(d,p) and MP2/6-311+G(d,p)) Calculations

	benzoic acid		2-hydroxybenzoic acid	
conformers[a]	HF (kJ/mol)	MP2 (kJ/mol)	HF (kJ/mol)	MP2[b] (kJ/mol)
1	0.0	0.0	0.0	0.0
2	33.8	25.0	13.7	11.7
3			40.5	
4			42.9	
5			34.5	
6			71.3	
7			40.6	

[a] The two low-energy conformers are depicted in Figures 5 and 6 for benzoic acid and 2-hydroxybenzoic acid, respectively. [b] MP2 calculations only were performed for the two low-energy forms.

phenyl ring and the O−H eclipsing the C═O bond and the second a higher-energy form (by 25 kJ mol^{-1} (MP2)) (see Table 3) has the O−H and C═O eclipsed and the carboxyl group approximately 30° out of the plane of the phenyl ring. It was only necessary to include the low-energy form in the model used in the electron diffraction analysis. The two conformers are depicted in Figure 5, which also shows the atom-numbering scheme.

2-Hydroxybenzoic Acid (salicylic acid). Theoretical calculations, using the Hartree−Fock level of theory, gave evidence for seven stable conformers for 2-hydroxybenzoic acid, one of which was at markedly lower energy than the others. The energy difference between the lowest conformer and the next lowest was found to be 11.7 kJ mol^{-1} (MP2). This form has the carboxyl group coplanar with the phenyl ring, the O−H group eclipsing the C═O bond of the carboxyl group and C═O of the carboxyl group oriented toward the O−H on the phenyl ring. In the model for the electron diffraction analysis, it was only necessary to include the lowest energy form. The energy differences between all the conformers are given in Table 3, and the two low-energy conformers are depicted in Figure 6.

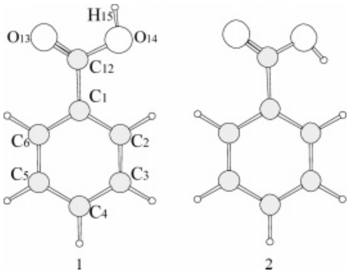

Figure 5. Diagram showing the conformers of 2-hydroxybenzoic acid (**1** 0.0 kJ mol^{-1} and **2** 25.0 kJ mol^{-1} (MP2)) and the numbering scheme.

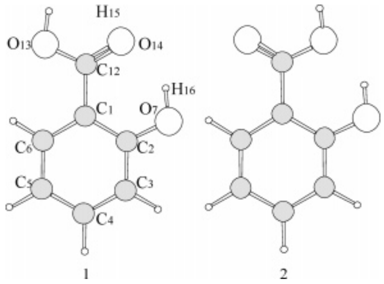

Figure 6. Diagram showing the two low-energy conformers of 2-hydroxybenzoic acid (**1** 0.0 kJ mol^{-1} and **2** 11.7 kJ mol^{-1} (MP2)) and the numbering scheme.

The structures of benzoic acid and 2-hydroxybenzoic acid were defined in terms of 21 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 with use of the SARACEN method.[14,15] Of the independent parameters, 8 and 10 were unrestrained in the refinements of the data for benzoic acid and 2-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 Figures 1 and 2, respectively, for benzoic acid and 2-hydroxybenzoic acid, together with experimental and difference curves. Figures 3 and 4 contain the corresponding RD-curves, and the correlation matrices for the refined parameters are given in Table 5.

Results and Discussion

The bond lengths (r_a), bond angles, and torsions from the electron diffraction analysis are listed in Table 4.

In the low-energy form of benzoic acid, the carboxyl group is coplanar with the phenyl ring. The carboxyl group causes little distortion of the C_6 ring from the symmetry seen in benzene. The C−C ring bond lengths (r_a) vary slightly within the range 1.396(2) to 1.403(2) Å with an average value of 1.400(2) Å. This mean value is slightly longer than that seen in the structure of crystalline benzoic acid[16] (1.388(6) Å) and very close to that found in the vapor-phase structure of benzene itself

TABLE 4: Structural Parameters Obtained from Electron Diffraction (GED) Refinements and Theoretical Calculations (MP2/6-311+G(d,p)) for the Low-Energy Form of Benzoic Acid and 2-Hydroxybenzoic Acid

	benzoic acid				2-hydroxybenzoic acid			
parameter[a]	GED		ab initio	restraint	GED		ab initio	restraint
Independent Parameters								
	$r_\alpha/\angle_\alpha$		$r_e/\angle_e$		$r_\alpha/\angle_\alpha$		$r_e/\angle_e$	
$r(C_1-C_2)$	1.400 (2)		1.404		1.416 (3)		1.415	
$r(C_1-C_2)-(C_2-C_3)$	0.007 (1)		0.007	0.001	0.011 (6)		0.011	0.007
$r(C_1-C_2)-(C_3-C_4)$	0.002 (1)		0.002	0.001	0.023 (3)		0.024	0.003
$r(C_1-C_2)-(C_4-C_5)$	0.003 (1)		0.003	0.001	0.006 (6)		0.010	0.006
$r(C_1-C_2)-(C_5-C_6)$	0.005 (0)		0.005	0.001	0.023 (4)		0.025	0.004
$r(C_1-C_2)-(C_1-C_6)$	−0.001 (1)		−0.001	0.001	0.009 (6)		0.005	0.007
$r(C_1-C_2)-(C_1-C_{12})$	−0.075 (7)		−0.087	0.012	−0.046 (9)		−0.058	0.015
$r(C_{phenyl}-H)$[b]					1.064 (13)		1.086	
$r(C_{12}=O_{13})$	1.220 (6)		1.213		1.224 (6)		1.227	
$r(C_{12}-O_{14})$	1.359 (8)		1.358					
$^1/_2[r(C_{12}-O_{14}) + r(C_2-O_7)]$[c]					1.330 (6)		1.348	
$r(C_2-O_7)-r(C_{12}-O_{14})$					0.005 (5)		0.001	0.005
$^1/_2[r(O_{14}-H_{15}) + r(C_{phenyl}-H)]$	1.024 (9)		1.027					
$r(O_{14}-H_{15})-r(C_{phenyl}-H)$	−0.108 (10)		−0.118	0.011				
$^1/_2[r(O_7-H_{16}) + r(O_{14}-H_{15})]$					1.031 (20)		0.973	
$r(O_7-H_{16})-r(O_{14}-H_{15})$					0.008 (5)		0.008	0.005
$^1/_2(\angle C_2C_1C_6 + \angle C_1C_2C_3)$	119.6 (2)		120.0		119.9 (3)		119.4	
$\angle C_2C_1C_6-\angle C_1C_2C_3$	0.6 (5)		0.6	0.5	−0.4 (7)		0.8	0.8
$\angle C_1C_2C_3-\angle C_1C_6C_5$	−0.4 (1)		0.2	0.1	0.9 (5)		−1.4	0.4
$\angle C_6C_1C_{12}$	124.0 (11)		121.9		119.0 (12)		121.3	
$\angle C_1C_{12}O_{13}$	126.6 (16)		124.8		122.6 (9)		124.4	
$\angle C_1C_{12}O_{14}$	113.1 (15)		112.6		116.2 (11)		114.1	
$\angle C_1C_2O_7$					122.1 (14)		123.5	
$\angle CCH_{phenyl,ave}$	120.0		120.0		120.0		120.0	
$\angle C_2O_7H_{16}$					106.8 (3)		106.8	3.8
$\angle C_{12}O_{14}H_{15}$	105.7 (25)		105.5	2.8	105.5 (24)		105.8	2.6
$\Phi C_2C_1C_{12}O_{13}$	0		0		0		0	
$\Phi O_{13}C_{12}O_{14}H_{15}$	0		0		0		0	
ΦCCO_7H					0		0	
Dependent Parameters								
	$r_a/\angle_\alpha$	l_{exp}	l_{theo}		$r_a/\angle_\alpha$	l_{exp}	l_{theo}	
$r(O_7-H_{16})$					1.051 (20)	0.069	0.069	
$r(O_{14}-H_{15})$	0.983 (13)	0.067	0.067		1.063 (20)	0.068	0.068	
$r(C-H)_{phenyl}$	1.102 (8)	0.075	0.075		1.077 (13)	0.075	0.075	
$r(C_{12}=O_{13})$	1.225 (6)	0.035	0.035		1.228 (6)	0.038	0.038	
$r(C_2-O_7)$					1.333 (7)	0.044	0.044	
$r(O_{14}-C_{12})$	1.367 (8)	0.033	0.033		1.339 (7)	0.044	0.044	
$r(C_1-C_2)$	1.402 (2)	0.055 (6)	0.044		1.419 (3)	0.050 (4)	0.047	
$r(C_2-C_3)$	1.396 (2)	0.054 (6)	0.043		1.407 (6)	0.050 (4)	0.047	
$r(C_3-C_4)$	1.402 (2)	0.054 (6)	0.043		1.395 (4)	0.050 (4)	0.047	
$r(C_4-C_5)$	1.401 (2)	0.054 (6)	0.043		1.413 (6)	0.050 (4)	0.047	
$r(C_5-C_6)$	1.400 (2)	0.054 (6)	0.043		1.396 (4)	0.050 (4)	0.047	
$r(C_1-C_6)$	1.403 (2)	0.055 (6)	0.044		1.410 (6)	0.050 (4)	0.047	
$r(C_1-C_{12})$	1.484 (6)	0.047	0.047		1.465 (8)	0.049	0.049	
$r(O_{13}-H_{16})$					1.727 (14)	0.155	0.155	
$\angle C_1C_2C_3$	119.3 (2)				120.0 (3)			
$\angle C_2C_3C_4$	121.9 (2)				120.8 (3)			
$\angle C_3C_4C_5$	117.9 (2)				118.5 (3)			
$\angle C_4C_5C_6$	121.4 (2)				122.0 (3)			
$\angle C_1C_6C_5$	119.7 (2)				119.1 (3)			
$\angle C_2C_1C_6$	119.9 (2)				119.6 (3)			

[a] Distances are in angstrøms (Å), and angles are in degrees (°); the uncertainties are given as 1σ and include systematic errors. [b] For benzoic acid, $r(C_{phenyl}-H)$ is refined with $r(O_{14}-H_{15})$. [c] For 2-hydroxybenzoic acid, $r(C_{12}-O_{14})$ is refined with $r(C_2-H_7)$.

(cf. benzene $r_a = 1.3971(18)$ Å[17]). The ring angles vary between 117.9(2)° and 121.9(2)°. The carbonyl C═O bond length ($r_a = 1.225(6)$ Å) is slightly longer than that found in the vapor-phase structure of benzaldehyde[1] ($r_a = 1.210(1)$ Å), and its length is closer to that found in 2-hydroxybenzaldehyde[1] ($r_a = 1.223(2)$ Å).

Of the seven conformers predicted for 2-hydroxybenzoic acid by ab-initio calculations, the lowest-energy form has the carboxyl group coplanar with the phenyl ring, the O−H group eclipsing the C═O bond of the carboxyl group and C═O of the carboxyl group oriented toward the O−H on the phenyl ring. In 2-hydroxybenzoic acid, the ring bond angles vary from 118.5(3)° to 122.0(3)° and the ring C−C bond lengths (r_a) vary from 1.395(4) to 1.419(3) Å. The average C−C value in 2-hydroxybenzoic acid ($r_{a(mean)} = 1.407(4)$ Å) is slightly longer than that found here for benzoic acid (1.400(2) Å). A similar observation

TABLE 5: Correlation Matrices for Benzoic Acid and 2-Hydroxybenzoic Acid[a]

Benzoic Acid

parameter	$r(C_{12}-O_{14})$	$r(O_{14}-H_{15})-r(C_{phenyl}-H)$	$\angle C_1C_{12}O_{13}$	$\angle C_1C_{12}O_{14}$
$r(C_1-C_2)$	−69		−55	
$r(C_{12}-O_{14})$	100		69	
$^1/_2[r(O_{14}-H_{15}) + r(C_{phenyl}-H)]$		50		
$\angle C_1C_{12}O_{13}$			100	−88

2-Hydroxybenzoic Acid

parameter	$r(C_{phenyl}-H)$	$\angle C_1C_{12}O_{13}$	$\angle C_1C_{12}O_{14}$	$\angle CCO_7$	$\angle C_6C_1C_{12}$	$l(C_1-C_2)$
$^1/_2[r(C_{12}-O_{14}) + r(C_2-O_7)]$		55				79
$^1/_2[r(O_7-H_{16}) + r(O_{14}-H_{15})]$	−63					
$r(C_{phenyl}-H)$	100					
$\angle C_1C_{12}O_{13}$		100	−67		51	
$\angle C_1C_{12}O_{14}$			100	−59	−78	
$\angle C_1C_2O_7$				100	78	

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

TABLE 6: Comparison of Structural Features from Electron Diffraction in Various Phenolic and Non-phenolic Ring Systems

parameter[a]	phenol	benzoic acid	benzaldehyde	2-hydroxybenzaldehyde	2-hydroxybenzoic acid
$r(C_1-C_2)_{phenyl}$	1.397(3)	1.402(2)	1.398(5)	1.416(9)	1.419(3)
$r(C_2-O_7)_{phenolic}$	1.380(4)			1.360(7)	1.333(7)
$r(C{=}O)_{carboxyl}$		1.225(6)	1.210(1)	1.223(2)	1.228(6)
$r(C_{12}-O_{14})_{carboxyl}$		1.367(8)			1.339(7)
$\angle C_1-C_2-O_{phenolic}$	121.2(12)				122.1(14)
$(\angle C_1-C_2-C_3)_{phenyl}$	121.6(2)	119.3(2)			120.0(3)
references	18	this work	1	1	this work

[a] Distances (r_a) are in angstrøms (Å), and angles are in degrees (°); for the numbering see Figure 6.

was found with the related aldehydes, benzaldehyde and 2-hydroxybenzaldehyde.[1] In the gas-phase structures of these compounds, the mean ring C−C bond length was observed to be longer in the *o*-substituted aldehyde by 0.008(3) Å (($r_{a(mean)}$) = 1.405(3) Å in 2-hydroxybenzaldehyde compared with 1.397(3) Å in benzaldehyde).

Intramolecular Hydrogen Bonding. The main feature of interest within the two title molecules is the internal hydrogen bonding present in the hydroxyl-substituted carboxylic acid. The key structural feature which indicates the presence of hydrogen bonding is the nonbonded $O_{13}\cdots H_{16}$ distance. The $O_{13}\cdots H_{16}$ distance (r_a) of 1.727(14) Å found experimentally here is indicative of a positive interaction between the two groups and compares well with the equivalent distances found in 2-hydroxybenzaldehyde[1] (1.74(2) Å) and nitrophenol[2] (1.72(2) Å), two similar molecules reported to exhibit intramolecular hydrogen bonding. However, such distances are notoriously difficult to determine precisely by electron diffraction and are generally associated with high uncertainties. Such resonance-assisted hydrogen bonding also results in further structural changes in the rest of the molecule as compared with the parent benzoic acid, although these effects are not as marked as in the solid state. Although the carbonyl bond length does not show a significant increase in 2-hydroxybenzoic acid compared to that in benzoic acid ($r_a(C_{12}-O_{13})$ = 1.228(6) and 1.225(6) Å, respectively), there is a definite shortening of the exocyclic C−C bond. The value of $r_a(C_1-C_{12})$ is 1.465(8) Å in 2-hydroxybenzoic acid compared with 1.484(6) Å in benzoic acid; the difference (Δ) is equal to 0.019 Å. The effects are less marked than those seen in the analogous molecules 2-hydroxybenzaldehyde and benzaldehyde where the C═O difference was found to be 0.013 Å and the exocyclic C−C difference 0.020 Å. A further effect of the internal hydrogen bonding is a lengthening of the ring C−C distance between the two substituents. In the two molecules studied here, $r_a(C_1-C_2)$ in the unsubstituted ring adjacent to the carboxylic acid group is 1.402(2) Å, whereas in 2-hydroxybenzoic acid the equivalent C−C distance is longer by 0.017 Å. Again, this effect is comparable to that observed in the aldehyde compounds ($\Delta r_a(C-C)$ = 0.017 Å). The resonance structures resulting from the internal hydrogen bonding proposed here are depicted in Figure 7. A further effect of this interaction is a reduction in $-C_1C_{12}O_{13}$, the angle subtended by the carbonyl group of 2-hydroxybenzoic acid toward the hydroxyl group on the neighboring ring carbon atom. In the unsubstituted molecule, the angle $-C_1C_{12}O_{13}$ is 126.6(15)° whereas in 2-hydroxybenzoic acid the angle is slightly smaller (122.6(9)°) as a result of the interaction between the carbonyl oxygen atom and the hydrogen atom of the hydroxyl group. Additionally, the carboxylic single C−O bond distance ($r_a(C_{12}-O_{14})$) is shorter in the substituted 2-hydroxybenzoic acid (1.339(7) Å) than in the unsubstituted molecule (1.367(8) Å) as a result of charge donation from the oxygen lone pair to the electrophilic carbonyl carbon atom.

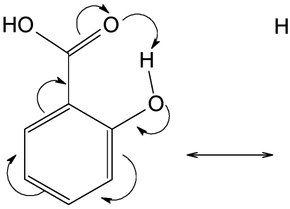

Figure 7. Proposed resonance structures resulting from the internal hydrogen bonding in 2-hydroxybenzoic acid.

A comparison of the pertinent structural features of various phenolic and nonphenolic ring systems is given in Table 6. From this it is clear that the phenolic C−O bond (r_a = 1.333(6) Å) is significantly shorter by 0.047 Å in 2-hydroxybenzoic acid than it is in phenol (r_a = 1.380(4) Å).[18] This shortening of the C−O bond is in agreement with the resonance structure invoked in Figure 7 which shows an increase in double-bond character as a result of the hydrogen bonding within the molecule.

Acknowledgment. This work has received support from The Research Council of Norway (Program for Supercomputing) through a grant of computing time. We thank Mr Alan Adams from the University of Reading for technical assistance and expertise. We thank Professor David Rankin and his research group of the University of Edinburgh for kindly providing access to his suite of programs and helpful discussions. Similarly, we also thank the electron diffraction group at the University of Oslo for supplying the data reduction program, the base for the high-temperature nozzle, and helpful discussions relating to the use of the image plates and reader.

References and Notes

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

(2) Borisenko, K. B.; Bock, C. W.; Hargittai, I. *J. Phys. Chem.* **1994**, *98*, 1442.

(3) Borisenko, K. B.; Bock, C. W.; Hargittai, I. *J. Phys. Chem.* **1993**, *97,* 4080.

(4) Borisenko, K. B.; Bock, C. W.; Hargittai, I. *J. Phys. Chem*. **1995**, *99*, 13808.

(5) Gilli, G.; Belucci, F.; Bertolasi, V. *J. Am. Chem. Soc.* **1989**, *111*, 1023.

(6) Bertolasi, V.; Gilli, P.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **1991**, *113*, 4917.

(7) Iwasaki, F.; Kawano, Y. *Acta Crystallogr. B* **1978**, *38*, 1286.

(8) Bourre-Maladiere, P. *C. R. Acad. Sci. (Paris)* **1953**, *237*, 825.

(9) Gdaniec, M. *Acta Crystallogr. C* **1991**, *47*, 1499.

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

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

(12) 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.

(13) 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 98, Revision A.11; Gaussian, Inc., Pittsburgh, PA, 2001.

(14) Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc*. **1993**, *160*, 117.

(15) 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.

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

(17) Bruno, G.; Randaccio, L. *Acta Crystallogr*. **1980**, *B36*, 1711.

(18) Tamagawa, K.; Iijima, T.; Kimura, M. *J. Mol. Struct*. **1976**, *30*, 243.

(19) Portalone, G.; Schultz, Gy.; Domenicano, A.; Hargittai, I. *Chem. Phys. Lett*. **1992**, *197*, 482.