Hydrogen Bonding in the Gas-Phase – The Molecular Structures of 2-Hydroxybenzamide (C$_7$H$_7$NO$_2$) and 2-Methoxybenzamide (C$_8$H$_9$NO$_2$), obtained by Gas-Phase Electron Diffraction and Theoretical Calculations.

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Abstract

The structures of 2-hydroxybenzamide (C$_7$H$_7$NO$_2$) and 2-methoxybenzamide (C$_8$H$_9$NO$_2$) 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 four stable conformers for both 2-hydroxybenzamide and 2-methoxybenzamide. For both compounds evidence for intramolecular hydrogen bonding is presented. In 2-hydroxybenzamide the observed hydrogen bonded fragment is between the hydroxyl and carbonyl groups while in 2-methoxybenzamide the hydrogen bonded fragment is between one of the hydrogen atoms of the amide group and the methoxy oxygen atom.

Keywords

Gas phase Electron diffraction, Ab initio, Structure, 2-hydroxybenzamide, 2-methoxybenzamide

Introduction

A gas-phase electron diffraction study on the substituted phenol 2-hydroxybenzaldehyde (salicylaldehyde)[1] revealed the existence of intramolecular hydrogen bonding. More recently we reported strong evidence for the existence of intramolecular hydrogen bonding

in gaseous 2-hydroxybenzoic acid.[2] The evidence was provided by a comparison of the gas-phase structure of 2-hydroxybenzoic acid with that of benzoic acid[2] and was further supported by a more recent study of 3-hydroxybenzoic acid and 4-hydroxybenzoic acid. [3] The most notable differences in the structure of 2-hydroxybenzoic acid compared to benzoic acid[2] are the shortening of the exocylic C-C bond, the shortening of the C-O single bond of the carboxyl group and the lengthening of the C-C ring bond between the two substituents. We were surprised at some of the differences we observed between the geometry of the carboxyl group in 2-hydroxybenzoic acid and that found in benzoic acid. Therefore, we decided to investigate the structural influence of replacing the OH fragment of the carboxyl group with an iso-electronic NH_2 group and so we now report the results of our studies of the gas-phase structures of 2-hydroxybenzamide and 2-methoxybenzamide. Our interest in 2-hydroxybenzamide was further stimulated by the single crystal X-ray diffraction study of it which provides evidence for intramolecular hydrogen bonding[4] of the type exhibited in gaseous 2-hydroxybenzoic acid. In addition, in the solid state structure of 2-hydroxybenzamide there is evidence for intermolecular hydrogen bonding in which the oxygen atom of one molecule is hydrogen-bonded to one of the hydrogen atoms of the NH_2 group of an adjacent 2-hydroxybenzamide molecule. This observation caused us to consider the possibility of observing intramolecular hydrogen bonding involving one of the hydrogen atoms from the NH_2 group and the methoxy oxygen atom in gaseous 2-methoxybenzamide where the oxygen atom of the methoxy group would provide the Lewis base lone pair. Single crystal X-ray diffraction studies of 2-methoxybenzamide and the equimolar complexes formed between 2-methoxybenzamide with urea and thiourea have been reported[5] and in each of the studies extensive hydrogen bonded networks were found that included evidence for intramolecular hydrogen bonding.

Experimental

Commercial samples of 2-hydroxybenzamide and 2-methoxybenzamide were obtained from the Sigma –Aldrich company 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 vapour. Experimental parameters,

namely temperatures, nozzle-to-plate distances, correlation parameters, final scaling factors and electron wavelengths for both compounds are listed in Table 1. Data reduction was performed using standard routines[6] employing published scattering factors.[7] Data analysis was carried out using the program "ed@ed". [8] The experimental intensity curves are shown in Figure 1. Radial distribution (RD) curves are presented in Figure 2.

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 Gaussian09 program[9], indicated that both 2-hydroxybenzamide and 2-methoxybenzamide exist as mixtures of four stable conformers (see Figures 3 and 4 respectively). The important geometrical parameters obtained from the theoretical calculations for the low energy forms are shown given in Supplementary material (Table S1) and the energy differences are given in Table 2.

Normal Coordinate Calculations

Vibrational data play an important part in the refinement of any model used to analyse 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[10,11] 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

In the theoretical models used in the electron diffraction refinement conformers that were found to be more than 10 kJ mol^{-1} higher in energy than that of the lowest energy conformer were not included. Thus the theoretical model used for 2-hydroxybenzamide contained only one conformer while that for 2-methoxybenzamide contained two. The

3

energy differences between all the conformers are given in Table 2 and the conformers are depicted in Figures 3 and 4.

Models for the gas-phase molecules of 2-hydroxybenzamide and 2-methoxybenzamide were designed. These structural models of 2-hydroxybenzamide and 2-methoxybenzamide were defined in terms of 27 and 34 independent geometrical parameters respectively (see Table 3). In the models employed all the C-H, N-H distances and CCH angles were assumed to be equal within each molecule. For 2-methoxybenzamide the structural parameters for the second conformer were constrained to the values of those obtained for the first conformer by values obtained by *ab initio* calculations (MP2/6-311+G(d,p)). Flexible restraints were used during refinements by use of the SARACEN method [12,13]. During the refinements of the data 15 and 17 of the independent parameters were unrestrained for 2-hydroxybenzamide and 2-methoxybenzamide respectively (see Table 3). Values for the major dependent parameters from the final refinements are given in Table 3.

Results and discussion

Ab initio calculations upon 2-hydroxybenzamide and 2-methoxybenzamide provided evidence for the existence of four stable conformers for each compound. The energy differences between the lowest energy conformer and those of the other three species for both compounds are recorded in Table 2. For 2-hydroxybenzamide the energy difference between the lowest energy conformer and the next lowest is 24 kJ mol^{-1}(Hartree Fock) and 20 kJ mol^{-1}(MP2) and so we confidently assumed that in the gas phase only the lowest energy form is present. This lowest energy conformer is depicted in Figure 3 together with the three high energy conformers. Figure 3 also contains the atom number scheme. A point worthy of note for the lowest energy conformer is that the $C_{12}=O_{13}$ vector is positioned to bring O_{13} relatively close to O_7. From Figure 3 it is apparent that the major geometrical difference between the lowest and the highest energy conformers for 2-hydroxybenzamide is the orientation of the hydroxyl group relatively to the C=O bond. The hydroxyl group is orientated toward the C=O for the lowest energy form and away from the C=O for the highest energy form. This difference could indicate the presence of a hydrogen bond between H_{17} and O_{13} in the lowest energy conformer that is absent in the highest energy

4

conformer. Thus the difference in energy between the lowest and highest energy forms could give some indication of the thermo-chemical strength of the hydrogen bond.

A different situation pertains with 2-methoxybenzamide (see Figure 4). From Table 2 it can be seen that the energy difference between the lowest and next lowest conformer is small (4 kJ mol^{-1} Hartree Fock; 1 kJ mol^{-1} MP2) with the third being 15 kJ mol^{-1} (Hartree Fock) and 10 kJ mol^{-1} (MP2) higher than the ground state. Thus for 2-methoxybenzamide we assumed that the two lowest energy conformers were present in the gas phase. In both of these conformers the $C_{12}=O_{13}$ vector is calculated to be a) in the plane of the aromatic ring but b) is orientated away from the methoxy substituent C_2-O_7. Thus, in these two conformers, N_{14}-H_{16} is brought relatively close to O_7 the oxygen atom of the methoxy group. Finally in the lowest energy conformer of 2-methoxybenzamide the chain N_{14}-C_{12}-C_1-C_2-O_7 is co-planar with the aromatic ring as can be seen from a consideration of the relevant torsion angles.

In Table 3 are recorded the structural parameters obtained from our gas-phase electron diffraction studies of 2-hydroxybenzamide and 2-methoxybenzamide. Also recorded in Table 3 are the results of *ab initio* calculations and there is good agreement between the results obtained from diffraction studies with those obtained by calculation. The aim of our study was to determine if 2-hydroxybenzamide and 2-methoxybenzamide exhibit intramolecular hydrogen bonding in the gas phase. In 2-hydroxybenzamide the potentially hydrogen bonded fragment is O_7-H_{17}...O_{13} and within this fragment the most accurately determined distance is the O_7..O_{13} distance which was found to be 2.594(24) Å (r_a) with the calculated value being 2.615 Å (r_e)(see Table 4). In the single crystal X-ray diffraction study of 2-hydroxybenzamide the comparable distance was reported as 2.513(1) Å .[4] We have shown that 2-hydroxybenzoic acid does show intramolecular hydrogen bonding within its O-H...O fragment and the O...O distance is 2.646(16) Å (r_a).[2] Thus, the O_7..O_{13} distance observed here supports the presence of an intramolecular hydrogen bond. Supporting, but not definitive, evidence was obtained from the values of the O_7-H_{17} and O_{13}...H_{17} distances (1.035(45) Å (r_a) and 1.617(82) Å (r_a) respectively). However, both values carry considerable uncertainty.

In our study of 2-methoxybenzamide, as stated above, we considered only the two lowest energy conformers. Our study showed that the second conformer (2 in Figure 4) formed only 11% of the mixture so we discuss only the structural features of conformer 1. Besides the replacement of the OH by OCH_3 the other major structural difference between 2-hydroxybenzamide and 2-methoxybenzamide is in the orientation of the amide group i.e. ($\{C_{12}=O_{13}\}$ -$N_{14}(H_n)_2$)(Figure 4, n = 15 or 16) which is rotated by about 180^0 relative to the C_2-O_7 bond, compared to the position observed in the lowest energy conformer of 2-hydroxybenzamide (Figure 3). The core of the amide group (i.e. C_1- $\{C_{12}=O_{13}\}$-N_{14}) is co-planar with the aromatic ring and the C_2-O_7 bond. This rotation brings the NH_2 fragment, and more particularly H_{16}, in relatively close proximity to O_7, which allows the possibility of intramolecular hydrogen bonding within the N_{14}-H_{16}...O_7 fragment. In this fragment the most accurately defined distance is the N_{14}...O_7 distance which was found to be 2.578(40) Å (r_a). As stated above single crystal X-ray diffraction studies have been reported for 2-methoxybenzamide and its I:I compounds formed with urea and thiourea.[5] It was reported that in the solid state all three compounds exhibited intramolecular hydrogen bonds involving N_{14} and O_7 with the distances being 2.771 Å for the pure compound and 2.638 Å and 2.661 Å for the equivalent distances in the urea and thiourea compounds respectively. However, no uncertainties were reported for these distances.[5] In gaseous 2-methoxybenzamide the O_7...H_{16} distance is 1.804(57) Å (r_a) which is in accord with a hydrogen bond being present between the two atoms but unfortunately the uncertainty on this distance is very high.

The intramolecular hydrogen bonds we propose in both the molecules under investigation can be considered to be part of six-membered rings which comprise $H_{17}O_7C_2C_1C_{12}O_{13}$ in 2-hydroxybenzamide (Figure 3) and $H_{16}O_7C_2C_1C_{12}N_{14}$ in 2-methoxybenzamide (Figure 4). It can be seen from the values of the torsion angles in Table 4 that both rings are planar. However, the relative positions of the hydrogen bonds in the two rings differ. In 2-hydroxybenzamide proceeding clockwise around the ring from the C_1-C_{12} bond shows this bond to be separated from the hydrogen bond by just one bond ($C_{12}=O_{13}$) (Figure 3). In 2-methoxybenzamide the C_1-C_{12} bond is separated from the hydrogen bond by two bonds

(C_{12}-N_{14} and N_{14}-H_{16}) (Figure 4). We suggest here that this has a consequence on some key bond lengths and angles in these six-membered rings.

There is no significant difference between the C_{12}-N_{14} distances in the two molecules studied here or that in gaseous benzamide[14] (Table 4). However, the distances are significantly shorter than the C-N distance observed in gaseous CH_3NH_2 (1.471(3) Å) where the nitrogen atom has a pyramidal co-ordination sphere[15] thus suggesting that there is some multiple bond character in C_1-N_{14} in both molecules . This suggestion is supported by the values of the four torsion angles ($\phi O_{13}C_{12}N_{14}H_n$ (n = 15 or 16)) reported in Table 4 which show that O_{13}, C_{12},N_{14}, H_{15} and H_{16} are co-planar in both molecules. Thus the nitrogen lone pair in each molecule is in a p orbital so facilitating some multiple bonding between C_{12} and N_{14}.

The C_{12}-O_{13} distance in 2-methoxybenzamide (1.190(5) Å) is significantly shorter than that in 2-hydroxybenzamide (1.230(6) Å). The relative lengthening of the C_{12} –O_{13} bond in 2-hydroxybenzamide can be ascribed to electron donation from O_{13} to H_{17} as part of hydrogen bond formation. The C_2-O_7 distances which are 1.336(5) Å in 2-hydroxybenzamide and 1.374(10) Å in 2-methoxybenzamide also differ significantly. The relatively short value in 2-hydroxybenzamide may be related to the weakening of the O_7-H_{17} bond as H_{17} takes part in hydrogen bonding so leading to a relative strengthening of C_2-O_7. Similar behaviour was found in gaseous 2-hydroxybenzoic acid (C_2-O_7 = 1.333(7) Å) but not in phenol (C-O = 1.380(4) Å) where no internal hydrogen bonding is present. [16]

In 2-hydroxybenzamide, the exocyclic C_1-C_{12} distance (1.494(4) Å) is slightly but not significantly shorter than that in benzamide (1.511(2) Å). We suggest but cannot state unequivocally that this is due to hydrogen bonding in the former molecule. However, a comparison of the equivalent exocyclic carbon-carbon distance of gaseous 2-hydroxybenzoic acid (1.465(8) Å) ,where internal hydrogen bonding was identified, with the same parameter in benzoic acid (1.484(6) Å)[2] showed it to be significantly shorter as a result of the intramolecular hydrogen bonding.

Of the pairs of comparable angles reported in Table 4 for 2-hydroxybenzamide and 2-methoxybenzamide there are significant differences between the values for $\angle C_{12}$-C_1-C_2 $\angle C_{12}$-C_1-C_6 and $\angle C_1$-C_2-O_7. The first two sets are related so consideration only needs to be given to the pairs of values for $\angle C_{12}$-C_1-C_2 and $\angle C_1$-C_2-O_7. In 2-hydroxybenzamide $\angle C_1$-C_2-O_7 ($123.5(15)^o$) is larger than $\angle C_{12}$-C_1-C_2 ($118.1(10)^o$) while in 2-methoxybenzamide the reverse is observed ($\angle C_1$-C_2-O_7 =$116.1(16)^o$ $\angle C_{12}$-C_1-C_2=$127.3(11)^o$). The pronounced differences between equivalent angles in the six-membered rings of each molecule must derive from the directionality and position of the internal hydrogen bond. In 2-hydroxybenzamide O_{13} is pulled towards H_{17} reducing $\angle C_{12}$-C_1-C_2 whereas in 2-methoxybenzamide the lone pair on O_7 donates electron density to H_{16} with an associated decrease in $\angle C_1$-C_2-O_7.

From the structural evidence presented here, and comparisons with related molecules, we conclude that intramolecular hydrogen bonding exists within the lower energy conformers of both the title molecules and could be responsible for their relative stabilities in the gas phase

Supporting Information Description

Table S1:

Results from the ab initio calculations (6-311+G(d,p) basis set) for 2-hydroxybenzamide ($C_7H_7NO_2$) and 2-methoxybenzamide ($C_8H_9NO_2$). For definition of conformers 1 and 2 see Figures 3 and 4.

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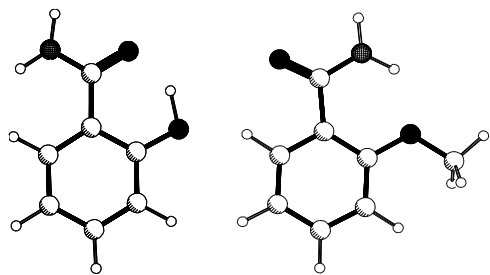
Table of contents

Table 1 Experimental Parameters for 2-hydroxybenzamide ($C_7H_7NO_2$) and 2-methoxybenzamide ($C_8H_9NO_2$).

	$C_7H_7NO_2$		$C_8H_9NO_2$	
nozzle to plate distance/mm	495.14	244.68	495.66	244.35
nozzle temperature/°C	140	155	130	130
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	3	3	3	3
s_{min}/$Å^{-1}$	3	8	3	8
s_{max}/$Å^{-1}$	14	29	13	28
s_{w1}/$Å^{-1}$	5	9	5	10
s_{w2}/$Å^{-1}$	12	25	11	24
Correlation parameter	0.4653	0.3178	0.205	0.380
Scale factor[a]	0.734(6)	0.830(20)	0.422(13)	0.438(18)

a) Values in parentheses are the estimated standard deviations

Table 2 Energy differences (kJmol^{-1}) between the different conformers for 2-hydroxybenzamide ($C_7H_7NO_2$) and 2-methoxybenzamide ($C_8H_9NO_2$) obtained from ab initio calculations (6-311+G(d,p) basis set). For definition of the conformers see Figures 3 and 4

Conformer	$C_7H_7NO_2$		$C_8H_9NO_2$	
	HF	MP2	HF	MP2
1	0	0	0	0
2	24	20	4	1
3	19	22	15	10
4	41	38	19	12

Table 3 Structural parameters obtained from electron diffraction (GED) refinements and theoretical calculations (MP2/6-311+G(d,p)) for 2-hydroxybenzamide ($C_7H_7NO_2$) and 2-methoxybenzamide ($C_8H_9NO_2$) (conformers 1 and 2, see Figures 3 and 4).

Independent parameters[a]	$C_7H_7NO_2$			$C_8H_9NO_2$		
	GED	Ab initio	Restraint	GED	Ab initio	Restraint
	r_{h1}	r_e		r_{h1}	r_e	
$r(C_1-C_2)$	1.424 (2)	1.416		1.421 (4)	1.416	
$r(C_1-C_2)-(C_1-C_{12})$	-0.072 (4)	-0.071	0.01	-0.073 (11)	-0.101	
$r(C_1-C_2)-(C_2-C_3)$	0.011 (5)	0.011	0.01	0.010 (9)	0.013	0.01
$r(C_1-C_2)-(C_3-C_4)$	0.023 (5)	0.023	0.01	0.022 (9)	0.004	0.01
$r(C_1-C_2)-(C_4-C_5)$	0.012 (5)	0.012	0.01	0.021 (9)	0.003	0.01
$r(C_1-C_2)-(C_5-C_6)$	0.023 (5)	0.023	0.01	0.018 (9)	0.001	0.01
$r(C_1-C_2)-(C_1-C_6)$	0.007 (5)	0.007	0.01	0.014 (9)	-0.008	0.01
$r(C_{12}=O_{13})$	1.232 (6)	1.237		1.191 (5)	1.227	
$1/2[r(C_{12}-N_{14})+r(C_2-O_7)]$	1.347 (4)	1.359		1.370 (10)	1.361	
$r(C_{12}-N_{14})-r(C_2-O_7)$	0.020 (5)	0.020	0.01	-0.011 (5)	-0.013	0.01
$1/2[r(N_{14}-H)+r(O_7-H_{17})]$	1.052 (44)	0.995				
$r(N_{14}-H)-r(O_7-H)$	0.028 (5)	0.028	0.01			
$r(N_{14}-H)_{ave}$				1.008 (20)	1.008	
$r(O_7-C_{17})$				1.413 (13)	1.411	
$r(C-H)_{ave}$	1.082 (14)	1.086		1.106 (7)	1.089	
$\angle C_1C_{12}=O_{13}$	120.1 (9)	121.8		121.8 (9)	120.5	
$\angle C_1C_{12}N_{14}$	118.8 (12)	117.1		115.5 (10)	117.4	
$\angle C_1C_2O_7$	123.5 (15)	123.0		116.1 (16)	117.9	
$\angle C_6C_1C_{12}$	122.7 (10)	122.3		114.8 (11)	114.9	
$1/2(\angle C_2C_1C_6+\angle C_1C_2C_3)$	119.2 (2)	119.3		118.9 (2)	119.1	
$\angle C_2C_1C_6-\angle C_1C_2C_3$	-0.2 (3)	-0.1	0.5	-0.6 (5)	-1.9	0.5
$\angle C_1C_2C_3-\angle C_1C_6C_5$	-1.9 (3)	-1.7	0.5	-1.8 (5)	-1.9	0.5
$\angle CCH_{phenyl}$	120.0	120.0		119.6 (9)		

	r_a	r_{h1}	r_e		r_a	r_{h1}	r_e	
∠$CN_{14}H_{15}$	110.9 (9)		115.1		116.9 (9)		117.0	[2]
∠$CN_{14}H_{16}$	119.2 (5)		119.2		122.5 (10)		117.7	[2]
∠$C_2O_7H_{17}$	105.6 (10)		105.9	[2]				
∠$C_2O_7C_{17}$					123.2 (17)		121.4	
∠$O_7C_{17}H_{ave}$					109.4 (9)		109.2	
φ$C_2C_1C_{12}=O_{13}$ [b]	-15 (5)		-19		-180		-180	
φ$C_1C_{12}N_{14}H_{15}$ [b]	-180 (1)		-171		-180		-180	
φ$C_1C_2O_7H_{17}$ [b]	-170 (4)		-172					
φ$C_1C_2O_7C_{17}$ [b]					-180		-180	
φ$C_2O_7C_{17}H_{20}$ [b]					-180		-180	
φ$C_2C_1C_{12}=O_{13}$ Conformer 2 [b]					-158		-158	
φ$C_1C_{12}N_{14}H_{15}$ Conformer 2 [b]					-174		-174	
φ$C_1C_2O_7C_{17}$ Conformer 2 [b]					105 (4)		103	[5]
φ$C_2O_7C_{17}H_{20}$ Conformer 2 [b]					-179		-180	
α conformer 1					89 (4)			

Important distances	r_a	r_{h1}	r_e	l_{theo}	r_a	r_{h1}	r_e	l_{exp}
$r(N_{14}-H)_{ave}$	1.065	1.066 (1)	1.060	0.067	1.005	1.008 (7)	1.007	0.068
$r(C-H)_{ave}$	1.078	1.082 (14)	1.086	0.074	1.003	1.006 (7)	1.089	0.074 (6)
$r(O_7-H_{17})$	1.035	1.038 (45)	0.981	0.067				
$r(C_{12}=O_{13})$	1.230	1.232 (6)	1.237	0.037	1.190	1.191 (5)	1.227	0.037 (6)
$r(C_{12}-N_{14})$	1.362	1.357 (5)	1.369	0.045	1.363	1.364 (10)	1.361	0.044 (6)
$r(C_2-O_7)$	1.336	1.337 (5)	1.349	0.043	1.374	1.376 (10)	1.374	0.044 (6)
$r(C_3-C_4)$	1.400	1.401 (5)	1.393	0.044	1.397	1.399 (9)	1.399	0.054
$r(C_5-C_6)$	1.400	1.401 (4)	1.393	0.044	1.401	1.403 (8)	1.395	0.054 (6)
$r(C_1-C_6)$	1.417	1.417 (4)	1.409	0.046	1.405	1.407 (8)	1.403	0.054 (20)
$r(C_2-C_3)$	1.412	1.413 (5)	1.405	0.046	1.409	1.410 (8)	1.403	0.055
$r(C_4-C_5)$	1.411	1.412 (4)	1.404	0.046	1.398	1.399 (9)	1.396	0.054
$r(C_{17}-O_7)$					1.410	1.411 (13)	1.423	0.047

r(C_1-C_2)	1.423	1.424	(2)	1.416	0.046	1.419 1.421 (4)	1.416	0.055
r(C_1-C_{12})	1.494	1.496	(4)	1.486	0.049	1.493 1.493 (10)	1.516	0.046
r(O_{13}·H_{17})	1.617	1.607	(82)	1.734	0.161			

a) Distances are in Ångstrøm (Å) and angles are in degree (^{o}). Uncertainties are given as 1σ.

b) Definition of torsion angles: $\phi C_2 C_1 C_{12}=O_{13}$ 0° when $C_{12}=O_{13}$ is eclipsing C_1-C_2, $\phi C_1 C_{12} N_{14} H_{15}$ 0° when N_{14}-H_{16} is eclipsing C_1-C_2, $\phi C_1 C_2 O_7 H_{17}$ 180° when O_7-H_{17} is eclipsing C_1-C_2, $\phi C_1 C_2 O_7 C_{17}$ 0° when O_7-C_{17} is eclipsing C_1-C_2, $\phi C_2 O_7 C_{17} H_{20}$ 180° when C_{17}-H_{20} is anti to C_2-O_7. Clockwise rotation gives negative torsion angles.

Table 4 Structural comparison of key distances and angles in 2-hydroxybenzamide and related molecules

Distances[a]	2-hydroxybenzamide[b]	2-methoxybenzamide[b]	benzamide[c]	2-hydroxybenzoic acid[e]
$r(C_{12}=O_{13})$	1.230(6)	1.190(5)	1.225(1)	1.228(6)
$r(C_1-C_{12})$	1.494(4)	1.493(10)	1.511(2)	1.465(8)
$r(C_{12}-N_{14})$	1.362(5)	1.363(10)	1.380(4)	
$r(C_1-C_2)$	1.423(2)	1.419(10)		1.419(3)
$r(C_2-O_7)$	1.336(5)	1.374(10)		1.333(7)
$r(O_7-H_{17})$	1.035(45)			1.051(20)
$r(O_{13}\cdots H_{17})$	1.617(82)			1.727(14)
$r(O_7\cdots H_{16})$		1.804(57)		
$r(O_7..O_{13})^d$	2.594(24) [2.615]			2.646(16) [2.637]
$r(O_7..N_{14})^d$		2.578(40) [2.766]		
Angles				
$\angle C_1-C_{12}=O_{13}$	120.1(9)	121.8(9)	121.2(5)	
$\angle C_{12}-C_1-C_2$	118.1 (10)	127.3(11)		
$\angle C_{12}-C_1-C_6$	122.7 (10)	114.8(11)		
$\angle C_1-C_2-O_7$	123.5(15)	116.1(16)		
$\angle C_1-C_{12}N_{14}$	118.8(12)	115.5(10)	117.8(5)	
$\angle C_2-O_7-H_{17}$	105.6(10)			
$\angle C_2-O_7-C_{17}$		123.2(17)		
Torsion angles				
$\phi O_{13}C_{12}N_{14}H_{15}$	0(1)	1(1)		
$\phi O_{13}C_{12}N_{14}H_{16}$	180(1)	178(1)		
$\phi C_2C_1C_{12}O_{13}$	14(5)	180		
$\phi C_{12}C_1C_2O_7$	0(0)	0(2)		
$\phi C_1C_2O_7H_{17}$	3(20)			
$\phi C_2C_7H_{17}O_{13}$	6(30)			
$\phi H_{16}N_{14}C_{12}C_1$		2(1)		
$\phi N_{14}C_{12}C_1C_2$		0(0)		
$\phi C_1C_2O_7H_{16}$		1(1)		

a) Distances are in Ångstrøm (Å), angles are in degree (°).

b) Gas phase. Distances are given as r_a and angles as $\angle_\alpha$. Uncertainties are σ. Data are from the present study

c) Gas phase. Distances are given as r_g and angles as $\angle_\alpha$. All ring C-C distances assumed equal. Uncertainties are σ. See reference 14

d) Values in square brackets were obtained from MP2/6-311+G(d,p) calculations

e) Gas phase see reference 2

Legends for Figures

Figure 1

Average experimental and theoretical intensity curves, $s^4 I_t(s)$, for 2-hydroxybenzamide and 2-methoxybenzamide

Figure 2

Radial distribution curves for 2-hydroxybenzamide and 2-methoxybenzamide. The difference curves are 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 $s\cdot\exp(-0.00002s^2)/(Z_N\text{-}f_N)(Z_O\text{-}f_O)$.

Figure 3

Representations of the four conformers of 2-hydroxybenzamide. The atom numbering scheme used is given on (1). The relative energies of these conformers are given in Table 2. Only the lowest energy form (1) was used in the refinement for the electron diffraction data.

Figure 4

Representations of the four conformers of 2-methoxybenzamide. The atom numbering scheme used is given on (1). Conformers (1) and (2) were used in the refinement of the electron diffraction data. The relative energies of these conformers are given in Table 2.
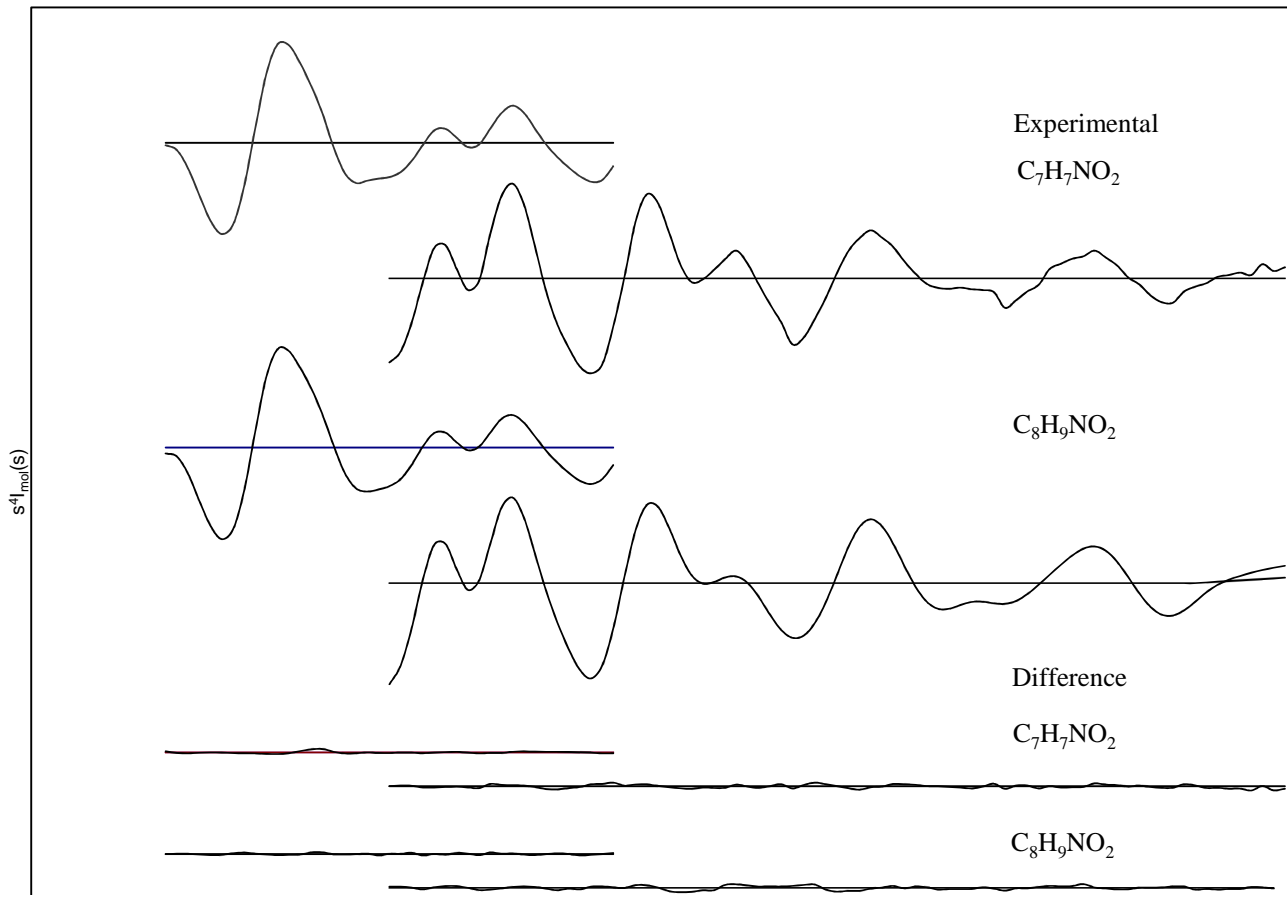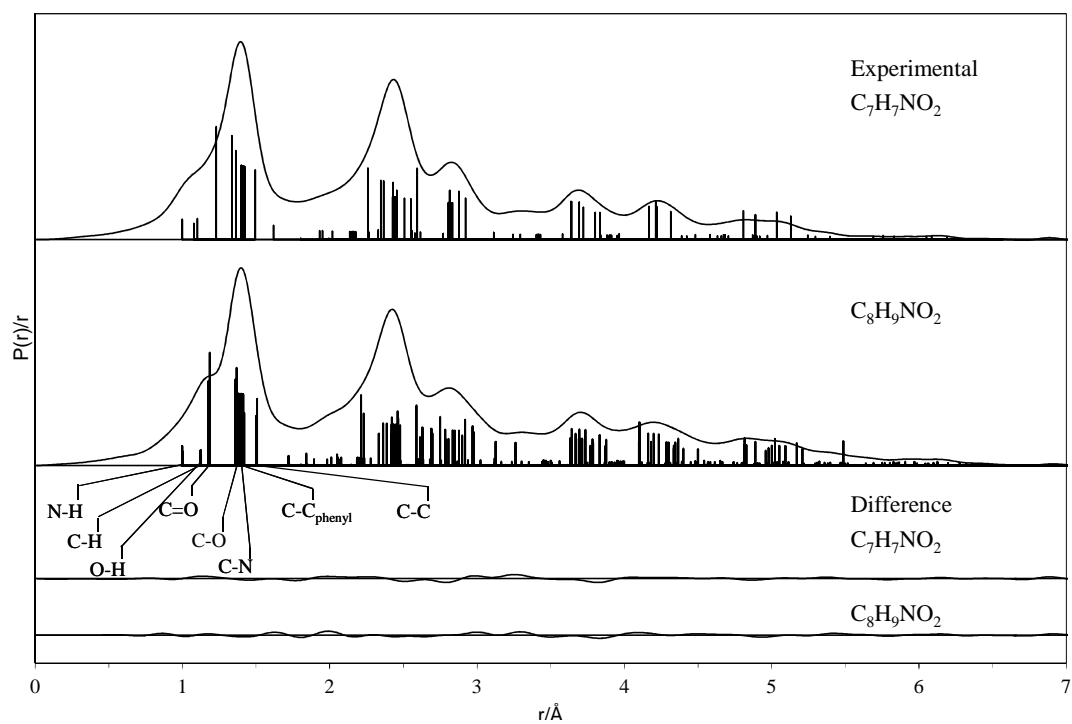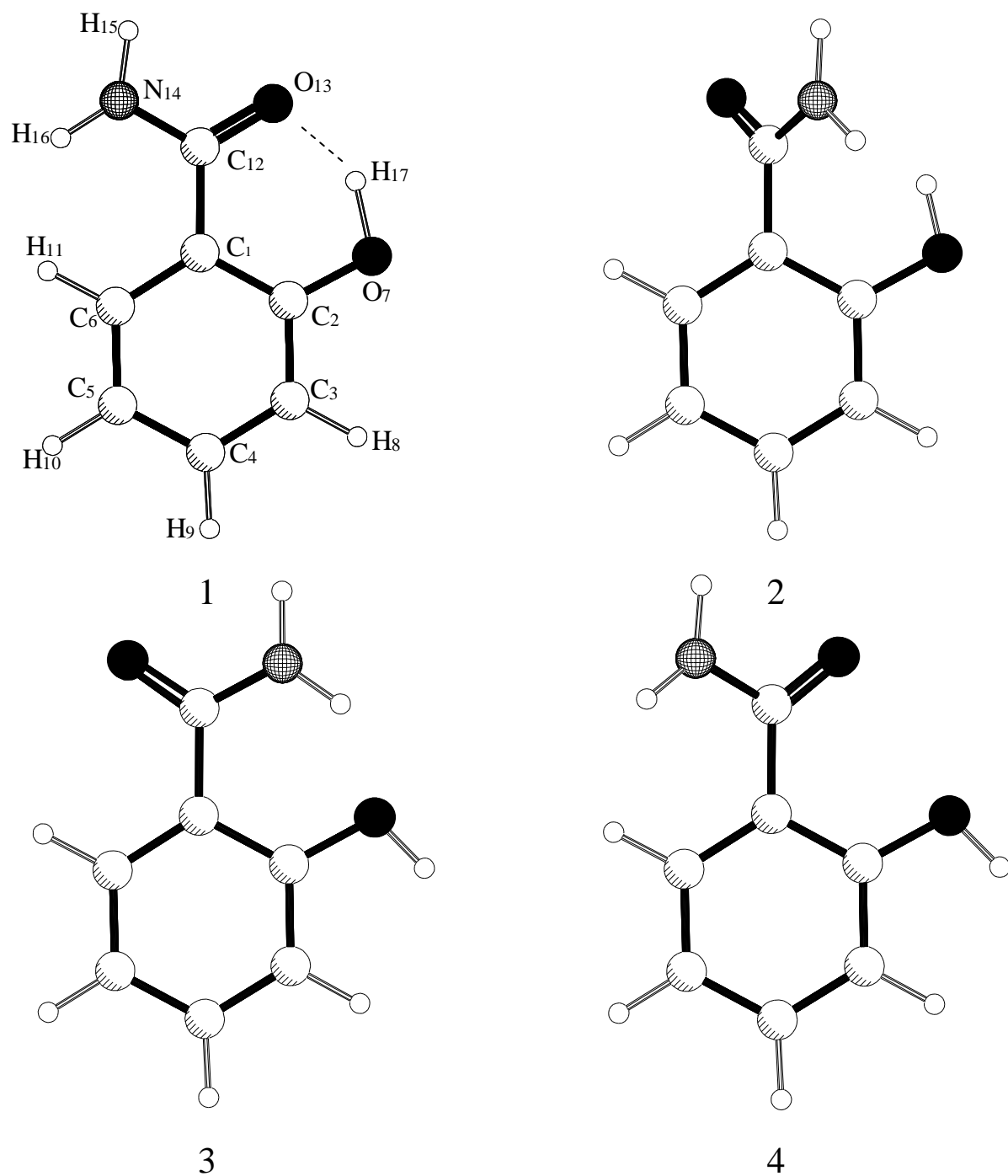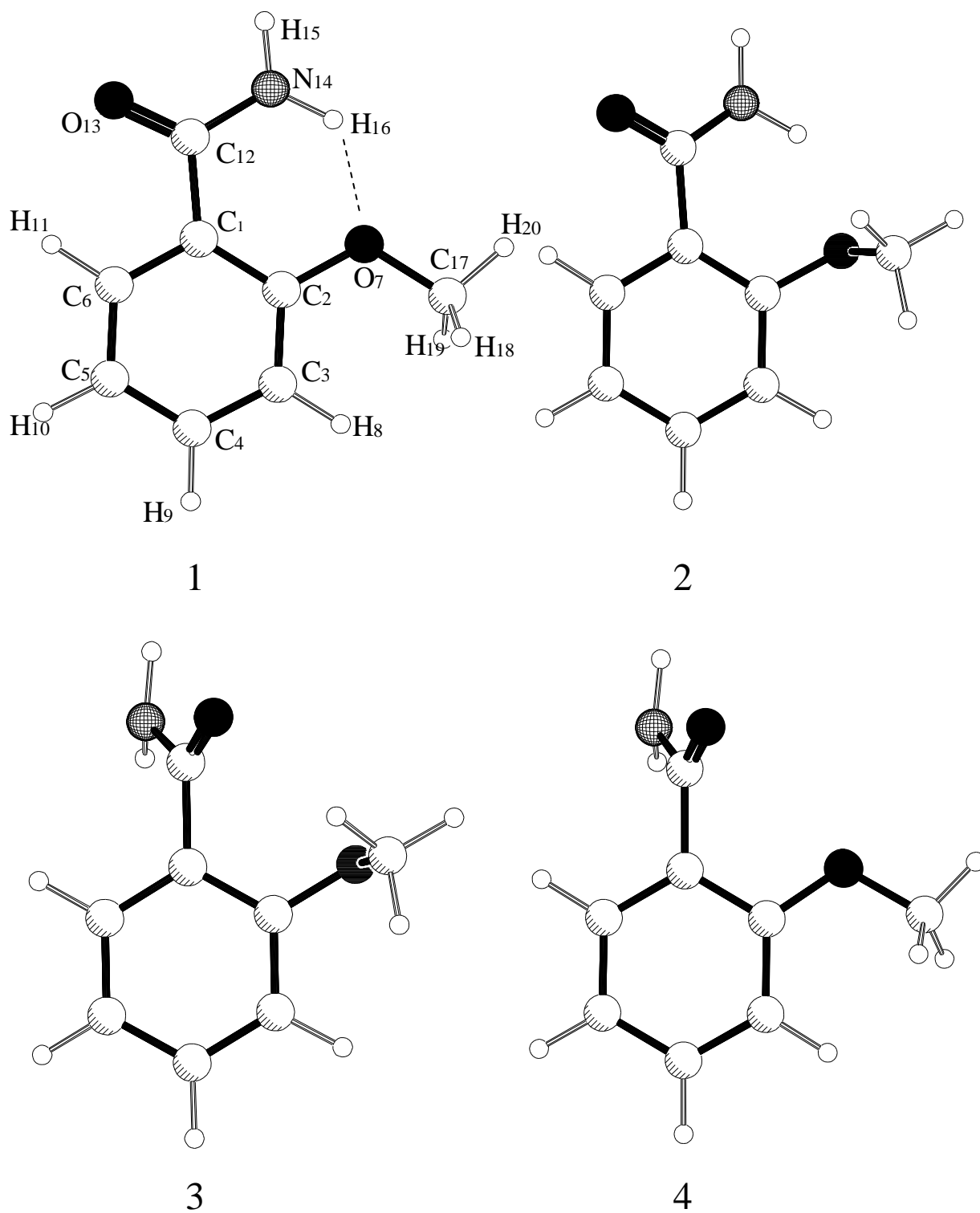
Figure 1

s^4 I_{mol}(s)

Experimental
$C_7H_7NO_2$

$C_8H_9NO_2$

Difference
$C_7H_7NO_2$

$C_8H_9NO_2$

18

Figure 2

1

2

3

4

Figure 3

1

2

3

4

Figure 4