Molecular Geometry of Benzaldehyde and Salicylaldehyde: A Gas-Phase Electron Diffraction and ab Initio Molecular Orbital Investigation

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Molecular Geometry of Benzaldehyde and Salicylaldehyde: A Gas-Phase Electron Diffraction and ab Initio Molecular Orbital Investigation

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The molecular geometries of benzaldehyde and salicylaldehyde have been determined by gas-phase electron diffraction and ab initio molecular orbital calculations at the MP2(FC)/6-31G* level. Several parameter *differences* from the molecular orbital calculations were incorporated as constraints in the electron diffraction analysis of salicylaldehyde. Some selected bond lengths (r_g) and angles obtained in the electron diffraction analyses are as follows: benzaldehyde $(C-H)_{mean}$ 1.095 ± 0.005 Å; $(C-C)_{mean}$ (benzene) 1.397 ± 0.003 Å; C_2-C_7 1.479 ± 0.004 Å; C=O 1.212 ± 0.003 Å; C_2-C_7=O 123.6 ± 0.4°; the benzene ring is undistorted within experimental error; salicylaldehyde $(C-H)_{mean}$ 1.090 ± 0.011 Å; $(C-C)_{mean}$ (benzene) 1.404 ± 0.003 Å; C_1-C_2 1.418 ± 0.014 Å; C−O 1.362 ± 0.010 Å; O−H 0.985 ± 0.014 Å; C_2-C_{13} 1.462 ± 0.011 Å; C=O 1.225 ± 0.004 Å; C_2-C_{13}=O 123.8 ± 1.2°; C_2-C_1-O 120.9 ± 1.1°. All the data are consistent with planar equilibrium structures for both molecules. The barrier to formyl group torsion is estimated to be appreciably higher for salicylaldehyde (at least 30 kJ/mol) than for benzaldehyde (at least 20 kJ/mol). There is intramolecular hydrogen bonding in the salicylaldehyde molecule of comparable strength with that in *o*-nitrophenol. The hydrogen bond is characterized by the following observed/calculated distances: O···H-(−O) 1.74(2)/1.80 Å and O···O 2.65(1)/2.68 Å. The structural changes in the rest of the molecule, as compared with the parent benzaldehyde and phenol molecules, are consistent with resonance-assisted hydrogen bonding similar to the *o*-nitrophenols. These changes include a lengthening of the C=O bond (0.013 Å), a shortening of the exocyclic C−C bond (0.020 Å), a lengthening of the ring C−C bond between the substituents (0.017 Å), and a shortening of the hydroxy C−O bond (0.022 Å).

Introduction

Our recent gas-phase electron diffraction studies of nitrophenols[2−4] have demonstrated intramolecular hydrogen bonding, as well as appreciable structural changes in the rest of the molecule as compared to the parent phenol[5] and nitrobenzene.[6] These results have been interpreted in terms of resonance-assisted hydrogen bonding[7] and were consistent with the results of ab initio molecular orbital (MO) calculations;[2,8] in fact, some of the calculated parameter differences were used as constraints in the electron diffraction analyses.[2,4] The general pattern of the structural features of gaseous 2-nitrophenol was in agreement with an X-ray crystallographic investigation.[9] Utilizing the information on benzene ring deformation from the structures of three substituted nitrophenols with intramolecular hydrogen bonding, viz., 2-nitrophenol, 2-nitroresorcinol, and 4,6-dinitroresorcinol, angular distortion parameters were estimated for the interacting nitro and hydroxy groups in the gaseous state.[4]

As a continuation of our research of the consequences of intersubstituent effects in ortho-substituted benzene derivatives, we have initiated the present study of the molecular structure of salicylaldehyde. Since one of its "parent" molecules, benzaldehyde, has never been studied by gas-phase electron diffraction, we decided to add it to the present investigation. Both of these molecules are of low symmetry, and a joint electron diffraction/ab initio investigation is preferable to an electron diffraction study only. Consequently, we decided to carry out ab initio MO calculations in conjunction with the experimental investigation, and to utilize the computed param-

eter differences as constraints in the analysis of the electron diffraction data, in a manner similar to that used previously.[2,4]

Benzaldehyde[10] and salicylaldehyde[11] have been studied by microwave spectroscopy. However, complete structural determinations were not possible because of the limited number of isotopomers available in these studies. This certainly contributed to the lack of any observed structural changes caused by intramolecular hydrogen bonding in salicylaldehyde.[11] A short O···H(−O) distance, 1.76 ± 0.01 Å, was reported, strongly suggesting considerable intramolecular interactions. An early low-temperature X-ray crystallographic study of salicylaldehyde[12] and a more recent one of a salicylaldehyde−gossypol complex[13] both indicated intramolecular structural changes, including a pronounced quinonoid form of the benzene ring.

Ab Initio MO Computations

Ab initio molecular orbital calculations on benzaldehyde and salicylaldehyde were carried out with the GAUSSIAN 92 series of programs.[14] The optimizations were performed with 6-31G* basis set[15] using second-order Møller−Plesset (MP2) perturbation theory[16] to incorporate the effects of electron correlation on the geometrical parameters of both structures, i.e., at the MP2(FC)/6-31G*//MP2(FC)/6-31G* computational level, where FC denotes that the frozen core option was used throughout. Vibrational frequency analyses were carried out to confirm that the computed planar structures were stable states indeed. Despite the availability of various quantum chemical computations of the geometries of benzaldehyde and salicylaldehyde,[17−19] we performed these calculations to produce a consistent set of structural data for comparison with our previous calculations

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TABLE 1: Benzaldehyde: Computed Geometries[a]

parameter	MP2(FC)/6-31G*[b]	HF/6-31G* (5D)[c]
C=O	1.2274	1.1907
C−H$_9$	1.1103	1.0942
C$_2$−C$_7$	1.4797	1.4822
C$_1$−C$_2$	1.4014	1.3926
C$_2$−C$_3$	1.3995	1.3881
C$_3$−C$_4$	1.3951	1.3862
C$_4$−C$_5$	1.3969	1.3852
C$_5$−C$_6$	1.3999	1.3902
C$_6$−C$_1$	1.3919	1.3814
C$_1$−H	1.0871	1.0735
C$_3$−H	1.0894	1.0765
C$_4$−H	1.0871	1.0744
C$_5$−H	1.0874	1.0755
C$_6$−H	1.0873	1.0749
∠O=C−H	120.53	120.37
∠C−C=O	124.23	124.50
∠C$_7$−C$_2$−C$_1$	119.94	120.27
∠C$_6$−C$_1$−C$_2$	119.59	119.97
∠C$_1$−C$_2$−C$_3$	120.34	119.85
∠C$_2$−C$_3$−C$_4$	119.86	120.23
∠C$_3$−C$_4$−C$_5$	119.83	119.67
∠C$_4$−C$_5$−C$_6$	120.23	120.34
∠C$_5$−C$_6$−C$_1$	120.14	119.94
∠C$_2$−C$_1$−H	118.75	118.98
∠C$_2$−C$_3$−H	119.79	119.88
∠C$_3$−C$_4$−H	120.11	120.12
∠C$_4$−C$_5$−H	119.87	119.84
∠C$_5$−C$_6$−H	119.88	120.01

[a] "r_e" equilibrium bond lengths (Å) and angles (deg). [b] Present work. [c] Reference 17.

TABLE 2: Salicylaldehyde: Computed Geometries[a]

parameter	MP2(FC)/6-31G*[b]	HF/6-31G** (5D)[c]
C=O	1.2399	1.201
C−H$_{15}$	1.1064	1.093
C$_2$−C$_{13}$	1.4597	1.465
O−H	0.9887	0.952
C−O	1.3527	1.328
C$_1$−C$_2$	1.4136	1.402
C$_2$−C$_3$	1.4064	1.399
C$_3$−C$_4$	1.3872	1.373
C$_4$−C$_5$	1.4028	1.396
C$_5$−C$_6$	1.3902	1.376
C$_6$−C$_1$	1.4010	1.394
C$_3$−H	1.0894	1.077
C$_4$−H	1.0861	1.074
C$_5$−H	1.0876	1.076
C$_6$−H	1.0863	1.074
O⋯H(−O)	1.8030	1.883
O⋯O(−H)	2.6805	2.694[d]
∠O=C−H	119.38	119.7
∠C−C=O	124.54	124.9
∠C$_{13}$−C$_2$−C$_1$	120.80	121.2
∠C$_2$−C$_1$−O	122.72	122.8
∠C−O−H	106.97	110.3
∠C$_6$−C$_1$−C$_2$	119.28	119.4
∠C$_1$−C$_2$−C$_3$	119.74	119.4
∠C$_2$−C$_3$−C$_4$	120.67	121.3
∠C$_3$−C$_4$−C$_5$	119.19	118.6
∠C$_4$−C$_5$−C$_6$	121.05	121.4
∠C$_5$−C$_6$−C$_1$	120.06	119.9
∠C$_2$−C$_3$−H	118.87	118.8
∠C$_3$−C$_4$−H	120.48	120.8
∠C$_4$−C$_5$−H	119.76	119.6
∠C$_5$−C$_6$−H	121.63	121.6

[a] "r_e" equilibrium bond lengths (Å) and angles (deg). [b] Present work. [c] Reference 18. [d] Calculated from data of ref 18.

on 2-nitrophenol.[2] It has also been our experience that high-level ab initio calculations which include the effects of electron correlation are essential for use in conjunction with good quality electron diffraction data on these types of structures. For example, some of the differences between the C−C bond lengths in the benzene ring of 2-nitrophenol,[2] calculated at the HF/6-31G* level, change signs when electron correlation is included in the optimization. The calculated differences obtained at the MP2(FC)/6-31G*//MP2(FC)/6-31G* level, however, are in good agreement with the X-ray crystallographic study of 2-nitrophenol.[9] Incidentally, even for the best calculated and experimental geometries, a comparison of structural parameters should focus on *differences* rather than absolute values, due to the inherent differences in the physical meaning of the parameters originating from various techniques.[20]

It is comforting to note, however, that the main features of the benzaldehyde and salicylaldehyde molecular geometries obtained in the present calculations are in agreement with those of earlier studies at different computational levels. Some results of recent calculations on benzaldehyde[17] and salicylaldehyde[18] are included in Tables 1 and 2 for comparison.

Electron Diffraction Experiment

The electron diffraction photographs of Aldrich Chemie commercial samples of benzaldehyde and salicylaldehyde were recorded in our modified EG-100A apparatus[21] with a membrane nozzle system[22] at two nozzle-to-plate distances, following purity checks by gas and liquid chromatography. Some of the experimental conditions for benzaldehyde and salicylaldehyde are summarized in Table 3. The coherent and incoherent atomic electron scattering factors were taken from available compilations.[23] The experimental and theoretical molecular intensities and radial distributions for both molecules are shown in Figures 1−4. The numbering of the atoms in our models is presented in Figure 5.
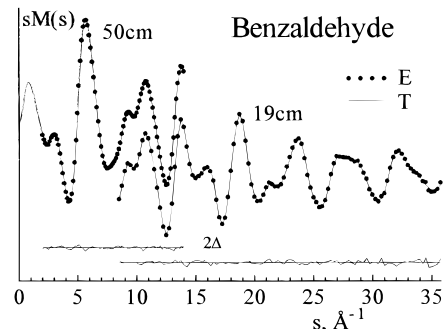

Figure 1. Experimental (E) and theoretical (T) molecular intensities and twice their differences (2Δ) for benzaldehyde.

TABLE 3: Electron Diffraction Experimental Conditions for Benzaldehyde and Salicylaldehyde

no. of plates	camera dist, mm	nozzle temp, °C	wavelength, Å	data interval, Å^{-1}	data step, Å^{-1}
			Benzaldehyde		
6	190.5	62	0.049 28	8.50−35.75	0.25
6	499.5	66	0.049 28	2.000−14.000	0.125
			Salicylaldehyde		
6	190.9	68	0.049 31	8.75−35.75	0.25
6	499.9	72	0.049 31	2.000−14.000	0.125

Structure Analysis

The analysis was carried out by the least-squares method, using the molecular scattering intensities[24] and applying the single start and the multistart Monte Carlo global optimization techniques.[25]

Benzaldehyde. Initially the molecule was assumed to have C_s symmetry, and the benzene ring to have local C_{2v} symmetry, with the 2-fold axis passing through the C$_2$ and C$_5$ carbon atoms.
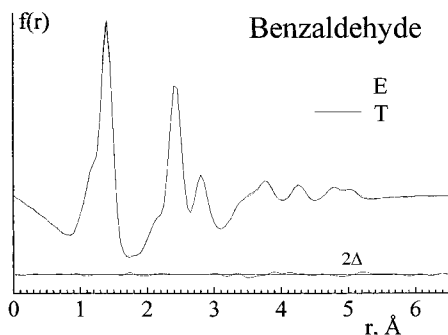
Figure 2. Experimental (E) and theoretical (T) radial distributions and twice their difference (2Δ) for benzaldehyde.
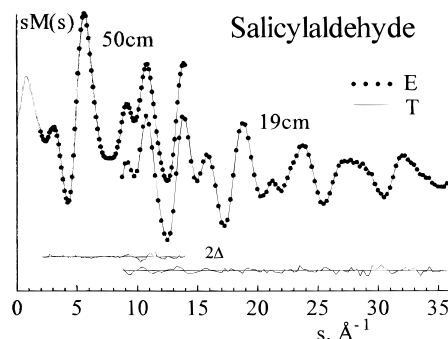

Figure 3. Experimental (E) and theoretical (T) molecular intensities and twice their differences (2Δ) for salicylaldehyde.
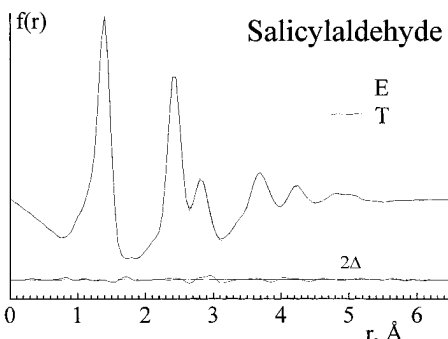

Figure 4. Experimental (E) and theoretical (T) radial distributions and twice their difference (2Δ) for salicylaldehyde.
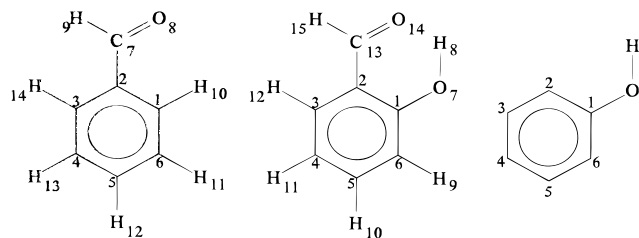

Figure 5. Numbering of atoms for the series benzaldehyde, salicylaldehyde, and phenol.

Actually, the results of the present ab initio calculations suggest that the C_{2v} point group is a rather good approximation for the benzene ring in benzaldehyde, since the differences between C−C bond lengths, related by the symmetry, do not exceed 0.003 Å. The overall symmetry of the molecule was lowered when torsion of the formyl group was investigated.

The benzene ring geometry was described by the following parameters: mean value of the ring C−C bonds, two ΔCC bond length differences (between C_1−C_2 and C_1−C_6, ΔCC1, and between C_1−C_2 and C_5−C_6, ΔCC2), and angles C_1−C_2−C_3 and C_2−C_1−C_6. All C−H bonds were assumed to have equal length and directed along the bisectors of the respective C−C−C
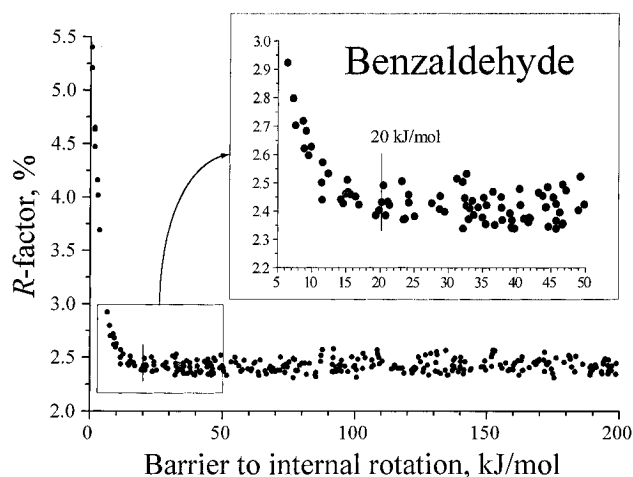

Figure 6. Graphical estimation of the barrier height to the internal rotation of the formyl group in benzaldehyde from the results of the Monte Carlo calculations with different assumed values of barrier height and initial geometries.

angles. Initially an attempt was made to refine the two ΔCC bond length differences independently. However, they refined to negative values, at variance with the results of the ab initio molecular orbital calculations. Thus these differences were assumed at different positive values in multistart Monte Carlo optimization with 1000 initial parameter sets in such a way that the value of the ΔCC2 difference was part of the ΔCC1 value. These differences, obtained in the least minimum from the Monte Carlo optimization, reproduced very closely those from the ab initio MP2(FC)/6-31G* calculations. Some vibrational amplitudes of C···C nonbonded distances in the benzene ring in the parameter set corresponding to the global minimum in the Monte Carlo optimization became too small, even smaller than the vibrational amplitudes of the C−C bonds. These amplitudes were then assigned values on the basis of experience with similar molecules and refined again. These changes had no appreciable influence on the *R*-factor and on the other parameters.

The geometry of the formyl group was described by the bond length differences, between the C_2−C_7 and the $(C−C)_{mean}$ bond lengths, ΔCC3; between the C=O and the $(C−C)_{mean}$ bond lengths, ΔCO; and between the C_7−H_9 and the $(C−H)_{mean}$ bond lengths, ΔCH, by the angle C_2−C_7=O, and by the deviation of the direction of the C_7−H_9 bond from the bisector of the C_2−C_7=O angle, ΔCCH. Varying the differences involving hydrogen atoms, i.e., ΔCH and ΔCCH, has led to suspiciously large values. Thus these parameters were also assumed in the Monte Carlo optimization at the calculated ab initio values, but were further varied as independent parameters in the final refinement.

The possibility of formyl group torsion was examined in the final stage of the analysis. Introduction of the angle of torsion for the formyl group in the refinement did not improve the agreement considerably and had no influence on the other parameters within experimental errors. The angle of formyl group torsion has refined to 7(7)°. Alternatively, we have performed a Monte Carlo optimization using a dynamic model concerning the internal rotation in benzaldehyde to estimate the barrier height to rotation of the formyl group. Assuming 2-fold potential function for such a rotation, $V(\phi) = (V_2/2)(1 - \cos(2\phi))$, the barrier height was graphically estimated to be at least 20 kJ/mol. The results of the calculations with different assumed barrier heights in the 0−200 kJ/mol interval and different initial geometries are presented in Figure 6. The graphical estimation of the barrier is somewhat arbitrary, but it

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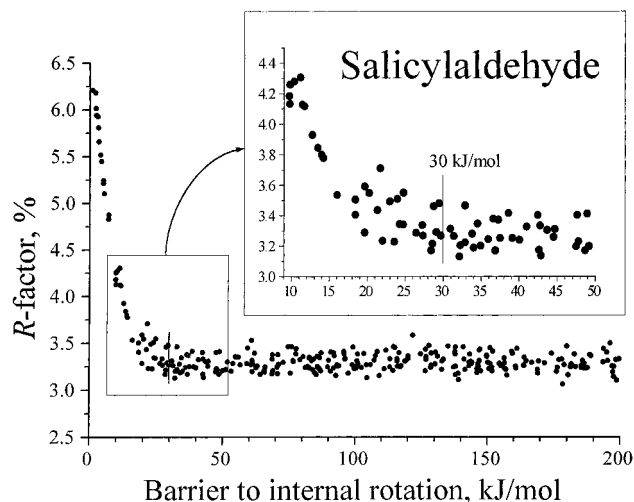
SCHEME 1

Figure 7. Graphical estimation of the barrier height to the internal rotation of the formyl group in salicylaldehyde from the results of the Monte Carlo calculations with different assumed values of barrier height and initial geometries.
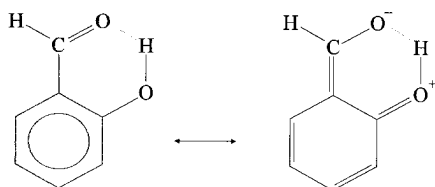
is independent of uncertainties in the determination of the structural parameters of the molecule.

Salicylaldehyde. The molecule was assumed to have C_s symmetry except when a torsional twist of the substituent groups was introduced. Some constraints have also been utilized from the ab initio MP2(FC)/6-31G* calculations (vide infra).

The benzene ring geometry was represented by the following independent parameters: C_1-C_2 bond length, four differences between C_1-C_2 and other C−C bond lengths, and four C−C−C angles. All C−H bonds were assumed to be of the same length and directed along the bisectors of the respective C−C−C angles. Considering the structures of 2-nitrophenol,[2] 2-nitroresorcinol,[3] and 4,6-dinitroresorcinol,[4] and also the ab initio calculations on salicylaldehyde, there should be an appreciable shortening of the C_3-C_4 and C_5-C_6 bonds with respect to the C−C bond in between the substituents and, to a lesser extent, with respect to the other C−C bonds. This may be ascribed to the contribution of the quinonoid resonance form (Scheme 1) to the overall structure, similar to that of *o*-nitrophenols with resonance-assisted intramolecular hydrogen bonding. Attempts to determine the individual C−C bond lengths by varying their differences in the least-squares refinements have not been successful. These refinements have led to a structure in which the C−C bond lengths were indistinguishable due to their relatively large standard deviations, or the differences obtained were in marked disagreement with expectations. Thus the computed differences were assumed in the final refinements.

The formyl group was described with the same parameter set as for benzaldehyde, and for the same reason, the differences ΔCH and ΔCCH were assumed at the calculated values throughout the analysis. Initially the C_2-C_{13} bond length (r_a) refined to 1.486(10) Å. This value has a large standard deviation and appears to be larger than the corresponding bond length in benzaldehyde, 1.477(2) Å. On the other hand, the ab initio calculations and previous experience with similar resonance interactions[2−4] suggested this bond to be considerably shorter than in the parent molecule, benzaldehyde. The benzene ring angles have always refined to values that made the C_4-C_5 bond even shorter than the C_3-C_4 and C_5-C_6 bonds, while the ab initio calculations predict these bonds to be the shortest in the benzene ring (Scheme 1). We have performed a Monte Carlo optimization with different assumed values of the benzene ring C−C−C angles, C_2-C_{13}, C−O, and C=O bond lengths, searching for the minimum which would satisfy certain conditions based on the structural variations expected for salicylaldehyde as compared to phenol and benzaldehyde. This approach also decreased the possible correlations between simultaneously refined parameters. The parameters of such a minimum were used as initial sets in subsequent calculations.

The hydroxy group was described with a ΔCO bond length difference between the C_1-C_2 bond and the C−O bond and with a ΔOH difference between $(C-H)_{mean}$ and the O−H bond. In addition, the C−O−H angle was refined as an independent parameter. The angle of torsion around the C−O bond could not be determined in the least-squares refinements, thus it was assumed to be zero, as suggested by the microwave spectroscopic study[11] and by the ab initio calculations.

At the final stage of the electron diffraction analysis, incorporating the constraints from the ab initio calculations, the possibility of formyl group torsion around the C_2-C_{13} bond was also examined. However, the refinement including such torsion did not converge; rather, it indicated continual rise of the *R*-factor. Assuming the formyl group angle of torsion at different values, the best agreement between the experimental and theoretical data occurs at 0° (corresponding to the shortest O···H distance). Furthermore, assuming this angle to be 180° not only caused a sharp increase of the *R*-factor but led to extreme changes in the calculated rotational constants, up to 20%. In the final stages of the analysis the angle of formyl torsion was assumed to be zero, which is consistent with the results of both the microwave spectroscopic study[11] and the ab initio calculations.

Calculations for the salicylaldehyde using a dynamic model were performed as well. The potential function in this case was assumed in the form $V(\phi) = (V_1/2)(1 - \cos(\phi))$. The results of Monte Carlo optimization with different assumed values of the barrier height, V_1, in the 0−200 kJ/mol interval and different initial geometries for salicylaldehyde are presented in Figure 7. Graphical estimation of the barrier height to internal rotation of the formyl group in salicylaldehyde gives at least 30 kJ/mol.

Refinement of the vibrational amplitudes for both molecules was performed according to the procedure previously discussed in the report about the application of the Monte Carlo global optimization method.[25]

The results of the final refinements are presented in Tables 4 and 5 for benzaldehyde and salicylaldehyde, respectively. For more realistic least-squares standard deviations, the ones listed in these tables were obtained in special calculations in which the assumed parameter differences were also treated as variables.

The rotational constants of benzaldehyde and salicylaldehyde calculated from the geometrical parameters of Tables 4 and 5, respectively, are also given in these tables along with the rotational constants determined from the microwave spectra for the normal species of benzaldehyde[10] and salicylaldehyde[11] in the ground state. Throughout the analysis the rotational constants have served as a gauge of the general consistency of the structures. However, they were not included in the refinement because, lacking vibrational corrections, this might have introduced systematic errors in the analysis. Table 6 lists the elements of the correlation matrices that exceed 0.6 in absolute value.

TABLE 4: Results of Electron Diffraction Least-Squares Refinement[a] of Benzaldehyde

type	r_a	l_a	group	type	r_a	l_a	group
				Independent Parameters			
$(C-C)_{mean}$	1.395(1)			ΔCCH^b	3(1)		
C_1-H_{10}	1.089(3)	0.080(1)	i	$\angle C_1-C_2-C_3$	119.9(7)		
$\Delta CC1^b$	0.008^d (5)			$\angle C_6-C_1-C_2$	120.2(10)		
$\Delta CC2^b$	0.001^d (16)			$\angle C_1-C_2-C_7$	120.9(4)		
$\Delta CC3^b$	0.082(2)			$\angle C_2-C_7=O$	123.6(3)		
ΔCO^b	0.185(1)			ϕ^c	7(7)		
ΔCH^b	0.020(22)						
				Dependent Distances and Angles			
C_1-C_2	1.398(5)	0.046	i	$C_1 \cdots H_{11}$	2.155(5)	0.105	ii
C_1-C_6	1.390(8)	0.045	i	$C_1 \cdots H_{12}$	3.393(5)	0.093	iv
C_5-C_6	1.397(12)	0.046	i	$C_1 \cdots H_{13}$	3.884(5)	0.129	iv
C_2-C_7	1.477(2)	0.047	i	$C_1 \cdots H_{14}$	3.407(16)	0.097	iv
$C=O$	1.210(1)	0.042	i	$C_2 \cdots H_9$	2.192(24)	0.099	ii
C_7-H_9	1.109(19)	0.086	i	$C_2 \cdots H_{10}$	2.158(9)	0.095	ii
$C_1 \cdots C_3$	2.421(16)	0.052	ii	$C_2 \cdots H_{11}$	3.405(4)	0.102	iv
$C_1 \cdots C_4$	2.795(4)	0.062	iii	$C_2 \cdots H_{12}$	3.869(10)	0.113	iv
$C_1 \cdots C_5$	2.407(5)	0.053	ii	$C_3 \cdots H_9$	2.642(28)	0.130	iii
$C_1 \cdots C_7$	2.501(6)	0.055	ii	$C_4 \cdots H_9$	4.029(26)	0.096	iv
$C_2 \cdots C_5$	2.780(9)	0.061(1)	iii	$C_5 \cdots H_9$	4.825(27)	0.125	vi
$C_2 \cdots C_6$	2.417(3)	0.053(1)	ii	$C_5 \cdots H_{10}$	3.396(5)	0.110	iv
$C_4 \cdots C_6$	2.429(18)	0.052	ii	$C_5 \cdots H_{11}$	2.162(14)	0.104	ii
$C_3 \cdots C_7$	2.480(6)	0.059	ii	$C_6 \cdots H_9$	4.606(24)	0.108	vi
$C_4 \cdots C_7$	3.761(4)	0.054	iv	$C_6 \cdots H_{10}$	2.151(12)	0.086	ii
$C_5 \cdots C_7$	4.258(8)	0.077(2)	v	$C_6 \cdots H_{12}$	2.155(13)	0.099	ii
$C_6 \cdots C_7$	3.775(4)	0.060(2)	iv	$C_6 \cdots H_{13}$	3.415(21)	0.115	iv
$C_1 \cdots O_8$	2.874(4)	0.086	iii	$C_6 \cdots H_{14}$	3.884(5)	0.103	iv
$C_2 \cdots O_8$	2.372(3)	0.055	ii	$C_7 \cdots H_{10}$	2.718(12)	0.124	iii
$C_3 \cdots O_8$	3.599(3)	0.063	iv	$C_7 \cdots H_{11}$	4.654(7)	0.100	vi
$C_4 \cdots O_8$	4.781(3)	0.070	vi	$C_7 \cdots H_{12}$	5.346(9)	0.147	vi
$C_5 \cdots O_8$	5.038(5)	0.076(3)	vi	$C_7 \cdots H_{13}$	4.633(6)	0.132	vi
$C_6 \cdots O_8$	4.260(8)	0.085	v	$C_7 \cdots H_{14}$	2.684(10)	0.117	iii
$O_8 \cdots H_9$	2.022(15)	0.097	ii	$\angle C_4-C_5-C_6$	120.7(5)		
$O_8 \cdots H_{10}$	2.603(10)	0.118	ii	$\angle C_1-C_6-C_5$	119.5(6)		
$O_8 \cdots H_{11}$	4.943(12)	0.116	vi	$\angle C_2-C_7-H$	115.1(11)		
$O_8 \cdots H_{12}$	6.110(5)	0.130^e		$\angle O=C-H$	121.2(11)		
$O_8 \cdots H_{13}$	5.727(6)	0.135^e		$CC,tilt^f$	0.8(4)		
$O_8 \cdots H_{14}$	3.889(7)	0.107	iv	R-factor	2.40%		
$C_1 \cdots H_9$	3.456(25)	0.119	iv				

Rotational Constants, MHz

	electron diffraction[g]	microwave spectroscopy[i]		electron diffraction[g]	microwave spectroscopy[i]
A	5223(2)	5234.28	C	1210(3)	1204.6988
B	1574(4)	1564.2411			

[a] Bond lengths, vibrational amplitudes in angstroms, angles in degrees. Least-squares standard deviations are parenthesized in units of the last digit. [b] $\Delta CC1 = r(C_1-C_2) - r(C_1-C_6)$, $\Delta CC2 = r(C_1-C_2) - r(C_5-C_6)$, $\Delta CC3 = r(C_2-C_7) - r(C-C)_{mean}$, $\Delta CO = r(C-C)_{mean} - r(C=O)$, $\Delta CH = r(C_1-H_{10}) - r(C_7-H_9)$, $\Delta CCH = 180.0 - C_2-C_7-H - (1/2)C_2-C_7=O$. [c] Angle of torsion around the C_2-C_7 bond. [d] Assumed in Monte Carlo optimization. [e] Assumed. [f] Positive when the $C_1-C_2-C_7$ angle is expanding. [g] Calculated from the above geometry. [i] Experimental values for the normal species in the ground state from the microwave spectroscopic investigation, ref 10.

Results and Discussion

The bond lengths (r_g), bond angles, and the angle of formyl torsion from the electron diffraction analysis, incorporating constraints from MP2(FC)/6-31G* ab initio calculations (salicylaldehyde), with estimated total errors, are listed in Tables 7 and 8 for benzaldehyde and for salicylaldehyde, respectively. Both systematic errors and least-squares standard deviations were included in the estimated total errors.[24] The parameters that are not listed in Tables 7 and 8 but appear in subsequent tables are also quoted with estimated total errors (e.g., angles of tilt).

Benzaldehyde. The geometry of the formyl group, taking into account the experimental errors, appears to be in satisfactory agreement with terephthalaldehyde;[27] for the latter, r_g(C−CHO) 1.487 ± 0.004 Å; r_g(C=O) 1.208 ± 0.003 Å; C−C=O 123.7 ± 0.4°. Even the minor differences may be meaningful as they appeared also in the results of the ab initio HF/6-31G calculations on the two molecules.[27] The C−CHO bond somewhat lengthens and the C=O bond shortens when going from benzaldehyde to terephthalaldehyde. An earlier electron diffraction study of the molecular structure of 2-chlorobenzaldehyde[28] reported 1.466 ± 0.021 Å for C−CHO, 1.195 ± 0.007 Å for C=O, and 120.0 ± 2.5° for C−C=O. The experimental errors are too large though for detailed comparison. Comparison with the results of more recent electron diffraction investigations of the molecular structures of *p*-anisaldehyde,[29] *p*-ethylbenzaldehyde, and *p*-isopropylbenzaldehyde[30] points to changes in the geometry of the formyl group caused by the introduction of a substituent in the para position.

An attempt to evaluate the benzene ring distortion under the impact of the formyl group as substituent was made in the paper reporting the electron diffraction structure of *p*-anisaldehyde.[29] Utilizing the results of the structure determination of only a single substance, the angular ring distortion parameters were estimated at $\Delta\alpha_{CHO}$, 0.2; $\Delta\beta_{CHO}$, −0.1; $\Delta\gamma_{CHO}$, −0.5; $\Delta\delta_{CHO}$, 1.0 (Scheme 2). The formyl group may also be looked at as an intermediate between the -COOH and -COCH$_3$ substituents, for which angular distortion parameters are available in the solid

TABLE 5: Results of Electron Diffraction Least-Squares Refinement[a] of Salicylaldehyde Incorporating Constraints (in Bold) from MP2(FC)/6-31G* ab Initio Calculation

parameter	r_a	l_a	group	parameter	r_a	l_a	group
				Independent Parameters			
C_1-C_2	1.416(9)	0.051(1)	i	ΔCCH	**1.6**[d] (25)		
C_6-H_9	1.083(8)	0.085	i	$\angle C_6-C_1-C_2$	120.9[e] (7)		
ΔCC1	**0.0126**[d] (221)			$\angle C_1-C_2-C_3$	118.2[e] (13)		
ΔCC2	**0.0234**[d] (253)			$\angle C_2-C_3-C_4$	121.5[e] (21)		
ΔCC3	**0.0072**[d] (208)			$\angle C_5-C_6-C_1$	118.9[e] (14)		
ΔCC4	**0.0264**[d] (235)			$\angle C_2-C_1-O$	120.9(8)		
ΔCO	0.056[e] (7)			$\angle C-O-H$	104.8(18)		
ΔOH	0.105(13)			$\angle C_1-C_2-C_{13}$	121.5(6)		
ΔCC5	0.044[e] (7)			$\angle C_2-C_{13}=O$	123.8(8)		
ΔCO2	0.193[e] (2)			τ^c	**0.0**[d]		
ΔCH	**0.019**[d] (407)			ϕ^c	**0.0**[d]		
				Dependent Distances and Angles			
C_2-C_3	1.409(13)	0.051	i	$C_6\cdots C_{13}$	3.795(11)	0.071	iv
C_3-C_4	1.390(21)	0.050	i	$C_2\cdots O_7$	2.414(15)	0.056	ii
C_4-C_5	1.402(29)	0.051	i	$C_3\cdots O_7$	3.678(11)	0.064	iv
C_5-C_6	1.393(30)	0.050	i	$C_4\cdots O_7$	4.164(10)	0.063	v
C_1-C_6	1.404(15)	0.051	i	$C_5\cdots O_7$	3.639(18)	0.065	iv
$(C-C)_{mean}$	1.402(1)			$C_6\cdots O_7$	2.371(20)	0.055	ii
C_2-C_{13}	1.460(7)	0.056	i	$C_{13}\cdots O_7$	2.876(15)	0.077	iii
C_1-O_7	1.360(7)	0.048	i	$C_1\cdots O_{14}$	2.886(16)	0.086	iii
C=O	1.223(2)	0.045	i	$C_2\cdots O_{14}$	2.369(12)	0.061	ii
O-H	0.978(10)	0.081	i	$C_3\cdots O_{14}$	3.622(13)	0.070	iv
$C_{13}-H_{15}$	1.102(34)	0.085	i	$C_4\cdots O_{14}$	4.806(9)	0.078(8)	vi
$C_1\cdots C_3$	2.426(19)	0.054(5)	ii	$C_5\cdots O_{14}$	5.054(8)	0.088(10)	vii
$C_1\cdots C_5$	2.408(15)	0.054	ii	$C_6\cdots O_{14}$	4.287(20)	0.095	v
$C_1\cdots C_4$	2.804(10)	0.063(2)	iii	$O_7\cdots O_{14}$	2.646(6)	0.086	ii
$C_2\cdots C_4$	2.442(9)	0.054	ii	$O_{14}\cdots H_8$	1.750(18)	0.099	i
$C_2\cdots C_6$	2.453(12)	0.054	ii	$\angle C_3-C_4-C_5$	119.0(8)		
$C_2\cdots C_5$	2.805(17)	0.063	iii	$\angle C_4-C_5-C_6$	121.5(11)		
$C_3\cdots C_5$	2.405(23)	0.055	ii	$\angle C_2-C_{13}-H_{15}$	116.5(26)		
$C_3\cdots C_6$	2.803(21)	0.063	iii	$\angle H-C=O$	119.7(24)		
$C_4\cdots C_6$	2.438(20)	0.054	ii	CC, tilt[f]	0.5(10)		
$C_1\cdots C_{13}$	2.508(7)	0.057	ii	CO, tilt[f]	1.3(9)		
$C_3\cdots C_{13}$	2.489(15)	0.059	ii	$\angle O-H\cdots O^g$	150.5(28)		
$C_4\cdots C_{13}$	3.772(9)	0.072(4)	iv	$\angle C=O\cdots H^h$	98.5(14)		
$C_5\cdots C_{13}$	4.264(14)	0.065(9)	v	R-factor	3.26%		

	Rotational Caonstants, MHz			
	electron diffraction[i]	microwave spectroscopy[j]		electron diffraction[i]	microwave spectroscopy[j]

	electron diffraction[i]	microwave spectroscopy[j]		electron diffraction[i]	microwave spectroscopy[j]
A	3217(13)	3215.97(6)	C	1015(1)	1020.110(4)
B	1484(3)	1493.618(4)			

[a] Bond lengths, vibrational amplitudes in angstroms, angles in degrees. Least-squares standard deviations are parenthesized in units of the last digit. Nonbonded distances including hydrogen atom are not shown, except that for the hydrogen bond. [b] ΔCC1 $= r(C_1-C_2) - r(C_1-C_6)$, ΔCC2 $= r(C_1-C_2) - r(C_5-C_6)$, ΔCC3 $= r(C_1-C_2) - r(C_2-C_3)$, ΔCC4 $= r(C_1-C_2) - r(C_3-C_4)$, ΔCO $= r(C_1-C_2) - r(C-O)$, ΔOH $= r(C_6-H_9) - r(O-H)$, ΔCC5 $= r(C_2-C_{13}) - r(C_1-C_2)$, ΔCO2 $= r(C_1-C_2) - r(C=O)$, ΔCH $= r(C_{13}-H_{15}) - r(C_6-H_9)$, ΔCCH $= 180.0 - C_2-C_{13}-H - (1/2)C_2-C_{13}=O$. [c] Angles of torsion, around the C_2-C_{13} bond, ϕ, and around the C-O bond, τ. [d] Assumed from the ab initio calculations (bold, present work). [e] Assumed in the Monte Carlo optimization. [f] Positive when tilt is away from the hydrogen bond. [g] Angle made by the O-H bond and the hydrogen bond. [h] Angle made by the hydrogen bond and the C=O bond. [i] Calculated from the above geometry. [j] Experimental values for the normal species from the microwave spectroscopic investigation, ref 11.

TABLE 6: Correlation Matrix Elements with Absolute Values Greater than 0.6 for Benzaldehyde and Salicylaldehyde

i	j	x_{ij}
	Benzaldehyde	
$\angle C_1-C_2-C_3$	$\angle C_6-C_1-C_2$	−0.9585
$\angle C_1-C_2-C_7$	ϕ	0.6886
$l(C_1-H_{10})$	$\angle C_1-C_2-C_3$	0.6624
	$\angle C_6-C_1-C_2$	−0.7375
$l(C_2\cdots C_6)$	$\angle C_1-C_2-C_3$	0.7774
	$\angle C_6-C_1-C_2$	−0.7384
	$\angle C_1-C_2-C_7$	−0.6364
	$\angle C_2-C_7=O$	0.6223
	$l(C_1-H_{10})$	0.6511
	Salicylaldehyde	
$\angle C_2-C_1-O$	$\angle C_1-C_2-C$	−0.6430
	$l(C_1\cdots C_3)$	−0.6495

TABLE 7: Bond Lengths (r_g, Å), Bond Angles, and the Angle of Torsion (deg) of Benzaldehyde with Estimated Total Errors from the Electron Diffraction Analysis

C_1-C_2	1.400 ± 0.007	$C_1-C_6-C_5$	119.5 ± 0.9
$(C-C)_{mean}$	1.397 ± 0.003	$C_4-C_5-C_6$	120.7 ± 0.7
$(C-H)_{mean}$	1.095 ± 0.005	$C_1-C_2-C_7$	120.9 ± 0.6
C_2-C_7	1.479 ± 0.004	$C_3-C_2-C_7$	119.2 ± 0.6
C=O	1.212 ± 0.003	$C_2-C_7=O$	123.6 ± 0.4
C_7-H_9	1.12 ± 0.03	C_2-C_7-H	115.1 ± 1.6
$C_1-C_2-C_3$	119.9 ± 1.0	O=C-H	121.2 ± 1.5
$C_6-C_1-C_2$	120.2 ± 1.4	ϕ^a	7 ± 10

[a] The angle of the formyl group torsion.

state.[31] Assuming the angular distortion parameters for the formyl group to be the arithmetic mean of the respective values for the -COOH and -COCH$_3$ groups, the following parameters can be obtained: $\Delta\alpha_{CHO}$, −0.5; $\Delta\beta_{CHO}$, 0.1; $\Delta\gamma_{CHO}$, 0.2; $\Delta\delta_{CHO}$, −0.1. The benzene ring angles of benzaldehyde may then be estimated as follows: $C-C_2-C$, 119.5°; $C-C_1-C$, 120.1°; $C-C_5-C$, 120.2°; and $C-C_6-C$, 119.9°.

All of the benzene ring angles of benzaldehyde appeared to

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TABLE 8: Bond Lengths (r_g, Å) and Bond Angles (deg) of Salicylaldehyde[a] with Estimated Total Errors from the Electron Diffraction Analysis Incorporating Constraints from MP2(FC)/6-31G* ab Initio Calculations

C_1-C_2	1.418 ± 0.014	$C_3-C_4-C_5$	119.0 ± 1.2
$(C-C)_{mean}$	1.404 ± 0.003	$C_4-C_5-C_6$	121.5 ± 1.5
$(C-H)_{mean}$	1.090 ± 0.011	$C_1-C_6-C_5$	118.9 ± 1.9
$C-O$	1.362 ± 0.010	C_2-C_1-O	120.9 ± 1.1
$O-H$	0.985 ± 0.014	$C-O-H$	104.8 ± 2.6
C_2-C_{13}	1.462 ± 0.011	$C_1-C_2-C_{13}$	121.4 ± 0.8
$C=O$	1.225 ± 0.004	$C_3-C_2-C_{13}$	120.4 ± 0.8
$C_{13}-H_{15}$	1.11 ± 0.05	$C_2-C_{13}-H$	116.5 ± 3.7
$C_6-C_1-C_2$	120.9 ± 0.9	$O=C-H$	119.7 ± 3.4
$C_1-C_2-C_3$	118.2 ± 1.8	$C-C=O_{14}$	123.8 ± 1.2
$C_2-C_3-C_4$	121.5 ± 2.9		

[a] All-planar model.

SCHEME 2

$$\Delta\alpha = \alpha - 120°$$
$$\Delta\beta = \beta - 120°$$
$$\Delta\gamma = \gamma - 120°$$
$$\Delta\delta = \delta - 120°$$
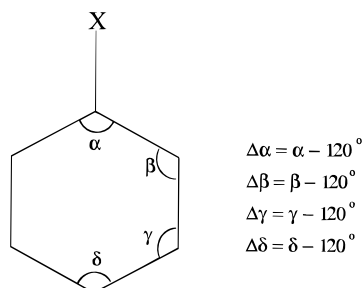
be hardly different from 120.0° (Table 7), taking into account their relatively large experimental errors, which, in turn, hinder a more detailed discussion of the angular deformations in benzaldehyde. Nevertheless, the geometry of benzaldehyde determined in the present investigation shows a slightly better agreement with the estimations based on the anisaldehyde structure than on the solid state geometries.

The mean value of $r_g(C-C)$ in the benzene ring of benzaldehyde, 1.397 ± 0.003 Å, appears to be the same, within experimental error, as in benzene itself,[32] 1.399 ± 0.003 Å, and also in some other monosubstituted benzene derivatives such as phenol,[5] 1.399 ± 0.003 Å.

The angle of the formyl group torsion, $7 \pm 10°$, does not indicate deviation from planarity within experimental error. Ab initio calculations as well as microwave spectroscopy[10] also suggest a planar equilibrium structure of benzaldehyde. The barrier to internal rotation, estimated from the effective angle of torsion and assuming a planar equilibrium conformation,[33] is rather high, 60 ± 171 kJ/mol, but very uncertain. Application of the dynamic model for internal rotation in benzaldehyde gives a barrier height of 20 kJ/mol, in excellent agreement with the values determined in microwave,[10] 20.5 ± 1.8 kJ/mol, and far infrared,[34] 19.3 kJ/mol, spectroscopic investigations.

Salicylaldehyde. There is resonance-assisted hydrogen bonding in salicylaldehyde similar to that found in 2-nitrophenol,[2] 2-nitroresorcinol,[3] and 4,6-dinitroresorcinol.[4] This suggests similar structural differences in salicylaldehyde as compared with benzaldehyde and phenol, as observed in the nitrophenol series and discussed previously.[2-4]

Benzene Ring Geometry. The mean value of the $C-C$ bond length in the benzene ring of salicylaldehyde, 1.405 ± 0.003 Å, appears to be slightly greater than the respective bond lengths in 2-nitrophenol,[2] 1.399 ± 0.003 Å, and benzene itself,[32] 1.399 ± 0.003 Å, but the differences are within experimental error. Interestingly, the X-ray crystallographic and the calculated ab initio $(C-C)_{mean}$ bond lengths of 2-nitrophenol and salicylaldehyde are in the same relationship, i.e., the $(C-C)_{mean}$ bond lengths in salicylaldehyde being slightly greater than those in 2-nitrophenol.

The $C-C$ bond length alternation in the benzene ring of salicylaldehyde as determined by the ab initio calculations is also consistent with the X-ray crystallographic observations in the solid state[12,13] and is a consequence of the substantial contribution of the *o*-quinonoid resonance form (Scheme 1) to the overall structure of salicylaldehyde.

The computed $C-C$ bond length differences in the benzene ring of salicylaldehyde are nearly the same as those for 2-nitrophenol,[2] while the internal benzene ring angles are quite different in these two molecules. Assuming the benzene ring internal angles of salicylaldehyde at the values of 2-nitrophenol caused a sharp increase in the *R*-factor. These differences between the $C-C-C$ angles in the two molecules originate from the different nature of the nitro group in 2-nitrophenol versus the formyl group in salicylaldehyde.

Formyl Group Torsion. The electron diffraction data are consistent with a zero or close to zero angle of the formyl group torsion in salicylaldehyde, in complete agreement with the results of the microwave study[11] and the present ab initio calculations. The barrier to internal rotation in salicylaldehyde, as obtained in the present study, is about 30 kJ/mol. The larger value, as compared to benzaldehyde, is obviously due to the restraining effect of the intramolecular hydrogen bonding. Consequently, one should expect a smaller effective angle of formyl group torsion in an electron diffraction analysis of salicylaldehyde than in that of benzaldehyde. The microwave spectroscopic study of salicylaldehyde[11] reports also the inertia defect for the normal species, whose negative value is probably due to the out-of-plane vibrations of the formyl and the hydroxy groups. The defect of inertia is only slightly different from zero, -0.091 amu Å^2, whereas the inertia defect for benzaldehyde[10] is -0.128 amu Å^2. Ignoring the hydroxy group torsional vibrations, since their contribution to the inertia defect should be marginal, the formyl group torsional angle corresponding to the inertia defect is estimated to be about 0.6°, lending further evidence to the planarity of the molecule.

Intramolecular Hydrogen Bonding. It is of special interest to compare the strength of the hydrogen bonding in the salicylaldehyde and 2-nitrophenol, as characterized by the distance of the nonbonded interaction $O\cdots H(-O)$ and the nonbonded $O\cdots O(-H)$ distance. The $O\cdots O(-H)$ distance increases by about 0.06–0.07 Å when going from 2-nitrophenol to salicylaldehyde, suggesting some weakening of the hydrogen bonding (2.58(1) and 2.616 Å for 2-nitrophenol,[2] 2.65(1) and 2.681 Å for salicylaldehyde from electron diffraction and ab initio calculations, respectively). The $O\cdots H(-O)$ distances are determined with large experimental errors from the electron diffraction studies (1.72(2) Å for 2-nitrophenol[2] and 1.74(2) Å for salicylaldehyde) and they do not appear different within experimental error, while the computed $O\cdots H(-O)$ distance is again shorter by 0.03 Å in 2-nitrophenol[2] (1.766 Å) than in salicylaldehyde (1.803 Å).

There has been an X-ray crystallographic determination of the molecular structure of salicylaldehyde in its complex with gossypol.[13] Comparison of the gaseous and crystalline molecular structures may be of interest in assessing possible consequences of intermolecular interactions in the crystal. However, before attempting any such comparison, all structural information must be reduced to the same physical meaning. This is done to avoid the so-called operational effects arising from the differences in the physical phenomena utilized in different techniques, including the difference in averaging over molecular vibrations. Lacking the necessary corrections, we restrict ourselves to some qualitative observations, namely, that the overall features of the salicylaldehyde molecular structure are

TABLE 9: Comparison of Phenol and Salicylaldehyde Geometrical Parameters from Electron Diffraction and MO Calculations[a]

parameter	electron diffraction			MO calculations MP2(FC)/6-31G*		
	phenol[b]	salicylaldehyde[c]	difference	phenol[d]	salicylaldehyde[e]	difference
C_1-C_2	1.399(3)	1.418(14)	+0.019	1.397	1.414	+0.017
O$-$H	0.958(3)	0.985(14)	+0.027	0.973	0.989	+0.016
C$-$O	1.381(4)	1.362(10)	-0.019	1.375	1.353	-0.022
C$-$O$-$H	106.4(17)	104.8(26)	-1.6	108.3	107.0	-1.3
C_2-C_1-O	121.2(12)	120.9(12)	-0.3	122.8	122.7	-0.1
$C_2-C_1-C_6$	121.6(2)	120.9(9)	-0.7	120.3	119.3	-1.0
CO, tilt	+2(1)	+1.3(13)	-0.7	+2.9	+2.3	-0.6

[a] Bond lengths in angstroms, angles in degrees. [b] Reference 5. [c] From the joint analysis incorporating constraints from MP2(FC)/6-31G* ab initio calculations, present work. [d] Reference 8. [e] Salicylaldehyde, ab initio calculations, present work.

TABLE 10: Comparison of Benzaldehyde and Salicylaldehyde Geometrical Parameters from Electron Diffraction and MO Calculations[a]

parameter	electron diffraction			MO calculations MP2(FC)/6-31G*		
	benzaldehyde	salicylaldehyde	difference	benzaldehyde	salicylaldehyde	difference
C_1-C_2	1.400(7)	1.418(14)	+0.018	1.401	1.414	+0.013
C$-$CHO	1.479(4)	1.462(11)	-0.017	1.480	1.460	-0.020
C=O	1.212(3)	1.225(4)	+0.013	1.227	1.240	+0.013
(C$-$H)$_{form}$	1.12(3)	1.11(5)	-0.01	1.110	1.106	-0.004
$\angle C_1-C_2-C$	120.9(6)	121.5(8)	+0.6	119.9	120.8	+0.9
$\angle$C$-$C=O	123.6(4)	123.8(12)	+0.2	124.2	124.5	+0.3
$\angle$O=C$-$H	121.2(15)	119.7(34)	-1.5	120.5	119.4	-1.1
$\angle$C$-C_2-$C	119.9(10)	118.2(18)	-1.7	120.3	119.7	-0.6
CC, tilt	+0.8(6)	+0.5(14)	-0.3	0.0	+0.6	+0.6

[a] Bond lengths in angstroms, angles in degrees.

the same in the gas and in the crystal. In particular, C$-$C bond length differences emerging from the MP2/6-31G* calculations are present in the crystal structure and consistency are found not only in the signs of the differences but even in their magnitudes. There seems to be a difference in the intramolecular O···O($-$H) distance in the gas, 2.65(1), and in the crystal, 2.61(2). The reduced distance in the crystal may be a consequence of the impact of molecular packing.

Comparisons of structural parameters of salicylaldehyde with those of phenol[5] and benzaldehyde both from electron diffraction and ab initio MO calculations are presented in Tables 9 and 10. There is a good general agreement between the structural variations determined by experiment and by calculations. They are similar to those observed in 2-nitrophenol[2] and 2-nitroresorcinol[3,8] as compared with nitrobenzene[6] and phenol.[5] However, the considerable shortening of the C$-$CHO bond in salicylaldehyde as compared to that of benzaldehyde was determined by the ab initio calculations only. This bond shortening was used as a constraint in the electron diffraction analysis (see the Structure Analysis section). The notion of this bond shortening is also supported by the increased barrier to torsion in salicylaldehyde as compared with that of benzaldehyde.

Conclusions

1. There is resonance-assisted intramolecular hydrogen bonding in salicylaldehyde. The geometrical changes, as compared with benzaldehyde and phenol, are similar to those in *o*-nitrophenols as compared with their parent molecules.

2. The structure analyses of benzaldehyde and salicylaldehyde have shown the utility of the Monte Carlo global optimization method in the refinement of structural parameters from gas-phase electron diffraction data.

3. The barriers to internal rotation of the formyl group, determined in the present study, indicated an increase of the barrier height in going from benzaldehyde to salicylaldehyde. This is probably due to the restraining effect of the intramolecular hydrogen bonding.

Supporting Information Available: Two tables showing total experimental electron diffraction intensities and background data for benzaldehyde and salicylaldehyde (8 pages). Ordering information is given on any current masthead page.

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