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Theoretical Study on Salicylaldehyde and 2-Mercaptobenzaldehyde: Intramolecular Hydrogen Bonding

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The molecular structures and the intramolecular hydrogen bonding for salicylaldehyde and 2-mercaptobenzaldehyde have been investigated with both ab initio and density functional theory methods. We have considered the several possible conformations with respect to the rotation of two functional groups in a given molecule not only to understand the conformational behaviors but also to estimate the energy of intramolecular hydrogen bonding. The optimized geometrical parameters for salicylaldehyde at the B3LYP levels and the computed ^{1}H NMR chemical shifts for 2-mercaptobenzaldehyde at the B3LYP/6-31+G* optimized geometry are in good agreement with those of previous experimental data. The results show that the inclusion of electron correlation at the B3LYP levels is more crucial in comparing the relative stability among the conformers of 2-mercaptobenzaldehede than among the conformers of salicylaldehede. The hydrogen-bonding energies are estimated by comparing the molecular energies between two different conformations either with a hydrogen bond or with no hydrogen bond of a given molecule. These energies for salicylaldehyde and 2-mercaptobenzaldehyde are computed to be about 9 and 2 kcal/mol at the B3LYP levels, respectively.

Introduction

Hydrogen bonding is an extremely important and useful concept for understanding various molecular properties of a system that has the possibility of an interaction between a hydrogen atom and a more electronegative atom such as F, O, and N. Intramolecular hydrogen bonding in particular is very responsible for the molecular conformation and intramolecular rearrangement of a certain molecule even though the strength of intramolecular hydrogen bonding is about a few kcal/mol, which is relatively weaker than an ordinary covalent bonding. This is the reason chemists not only study the behaviors of molecules with intramolecular hydrogen bonding but also try to estimate this weak interaction as precisely as possible. The traditional ways of predicting the strength of intramolecular hydrogen bonding are to assess the vibrational frequency shifts, such as OH-stretching and OH-torsion, in IR spectra and the chemical shifts of the hydroxyl protons in NMR spectra.

Some molecules with more than one intramolecular hydrogen bond of the same type, such as nitroresorcinol,[1−4] or with the possibility of two different types of intramolecular hydrogen bond according to a change of conformations in a molecule, such as 2-hydroxythiophenol and its derivatives,[5−7] are more attractive to chemists since the prediction of their molecular structures and conformational behaviors are much more complicated than those of the molecular structures with a simple hydrogen bond. However, since experimental approaches to these kinds of molecules are sometimes not enough to verify how much the molecular structure and conformation are affected by the hydrogen bond or to explain characteristics of the hydrogen bond for each type, the theoretical studies for these molecules in terms of molecular orbital are still demanded.

According to the results from previous theoretical studies,[2,8,9] the calculations of intramolecular hydrogen-bonding systems at the Hartree−Fock (HF) levels are not enough to predict their details of molecular properties such as the geometrical and conformational features. Therefore, post-Hartree−Fock approximations such as the second-order Moeller−Plesset perturbation (MP2) method are required to describe the molecular properties of such hydrogen-bonding systems more intensively. However, molecular orbital calculations with reliable basis sets larger than 6-31G* at this level of theory are still a formidable task for larger molecules. Recent theoretical studies[10−14] show that the density functional theory (DFT) is becoming an alternative to ab initio methods since it is sufficiently accurate and applicable to any system of interest, even for larger molecules. DFT is practically a much cheaper technique than conventional ab initio methods, especially in terms of the electron correlation. The results of previous studies[15−17] indicate that molecular properties calculated with the DFT methods are in excellent agreement with the available experimental data for benzene analogues as well as for systems containing the hydrogen bonding. According to the previous theoretical studies for 4,6-dinitroresorcinol[3] and 2-hydroxythiophenol,[7] DFT can also provide good results for systems with intramolecular hydrogen bonding.

Salicylaldehyde and its sulfur analogue, 2-mercaptobenzaldehyde, are very interesting examples because not only do they have the possibility of more than one different hydrogen-bonding conformer with respect to a change of conformation but they can also make a resonance-assisted hydrogen bonding.[9] According to the previous conformational study for these two molecules by Schaefer et al.,[18] the strength of hydrogen bonding for the most stable conformer of salicylaldehyde is quite different from that of 2-mercaptobenzaldehyde. However, among four possible conformers for 2-mercaptobenzaldehyde, two conformers are isoenergetic at the HF/6-31G** level while

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the molecular energies of all of four conformers for salicylaldehyde are apparently distinguished at this level. Moreover, all conformers calculated in the previous study have a geometrical restriction with a planar symmetry. Therefore, more precise investigation is still required in order to verify its conformational nature. More recently, an electron diffraction study along with an ab initio calculation at the MP2 levels for salicylaldehyde has also been performed.[19]

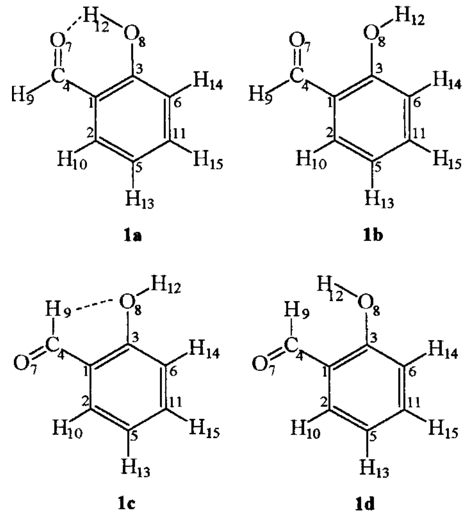
In this article, we are going to investigate both the molecular structures and the conformational nature for salicylaldehyde and 2-mercaptobenzaldehyde in terms of molecular orbitals by an ab initio method as well as the density functional theory. We compare the optimized geometrical parameters as well as ^1H chemical shifts with the experimental values and discuss the differences of calculated structural parameters between salicylaldehyde and 2-mercaptobenzaldehyde. In addition, we also discuss the structural differences among possible conformers of these two molecules in order to verify how much the intramolecular hydrogen bonding affects geometries of given molecules. Finally, we estimate the hydrogen-bonding energies for possible hydrogen-bonding conformers of these molecules by comparing the molecular energies among the conformers at the various levels of theory.

Computational Details

The molecular geometries of possible conformers for salicylaldehyde and 2-mercaptobenzaldehyde are fully optimized at the various levels of theory using the Gaussian 94 program[20] without any geometrical restrictions. All geometry optimizations have been performed first at the restricted Hartree−Fock (RHF) levels by using 6-31G**, 6-31+G*, 6-311G* basis sets. The effects of electron correlation on the geometry optimization are taken into account intensively by using Becke's three-parameter-hybrid (B3LYP) method[21−23] in the density functional theory with 6-31G**, 6-31+G*, and 6-311G* basis sets. This is because the B3LYP method provides energetics typically better than the HF method[22] and can reproduce better geometrical parameters, comparable to the experimental values, than any other method.[24] In addition, the B3LYP results are pretty close to correlated post-HF approximations such as the MP2 method or better.[25,26] Furthermore, the geometry optimization for 2-mercaptobenzaldehyde at the MP2/6-31G* level is also performed in order to make a more reliable comparison with its molecular structures at the B3LYP levels. Vibrational frequency analyses at the RHF/6-31G**//RHF/6-31G** indicate that optimized structures of all conformers are at stationary points corresponding to local minima without imaginary frequencies.

Results and Discussion

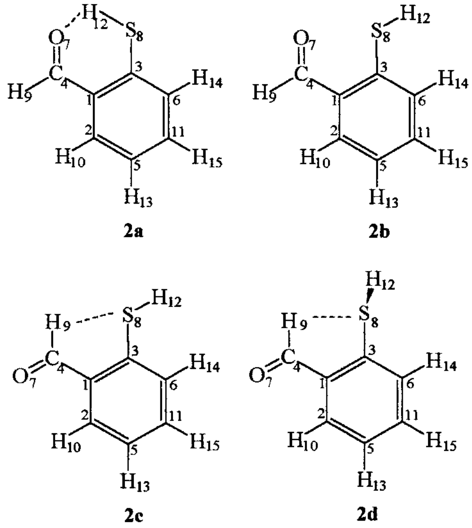
Molecular Structures of Salicylaldehyde and 2-Mercaptobenzaldehyde. The molecular geometries of possible conformers for salicylaldehyde and 2-mercaptobenzaldehyde are illustrated with the numbering of atoms in Figures 1 and 2, respectively. All conformers of both molecules are classified by the relative position of two neighboring substituents: CHO and OH in salicylaldehyde and CHO and SH in 2-mercaptobenzaldehyde. For salicylaldehyde, one can expect that both conformers **1a** and **1c** have a hydrogen bond between the hydrogen and oxygen atoms, while the other two conformers **1b** and **1d** have no hydrogen bond at all. However, the overlap population analyses show that there is no hydrogen bond in conformer **1c** since the bond distance O_8---H_9 (∼2.6 Å) is too long for intramolecular hydrogen bonding. On the other hand, among four conformers of 2-mercaptobenzaldehyde, three of them except for conformer **2b** can be expected to have the hydrogen bond. Among them, conformer **2d** is supposed to have somewhat characteristic interaction between hydrogen and sulfur atoms. For conformer **2d**, the sulfhydryl group S−H lies almost perpendicular to the benzene plane. This conformation will make us consider the possibility of the interaction between a 3p orbital of the sulfur atom and the 1s orbital of the hydrogen atom just as described in 2-hydroxythiophenol.[5,7] However, the overlap populations also show that hydrogen bonding rarely exists in conformer **2d** as well as in conformer **2c**.



1a **1b**

1c **1d**

Figure 1. Possible conformers of salicylaldehyde.



2a **2b**

2c **2d**

Figure 2. Possible conformers of 2-mercaptobenzaldehyde.

The results of geometry optimization at both RHF and B3LYP levels show that all four conformers of salicylaldehyde have C_s symmetry since CHO and OH substituents in all four conformers are located on the same plane as the benzene ring. In 2-mercaptobenzaldehyde, three conformers, **2a**, **2b**, and **2c,** also have a plane of symmetry. However, the S−H group of conformer **2d** is so much twisted out of the benzene plane that the torsional angle of the S−H group is computed to be approximately 90° at the RHF levels. This torsional angle, however, somewhat decreases at the B3LYP levels. In addition, the local minimum of a conformation with the S−H group syn to the C−H bond in the aldehyde group, which has C_s symmetry, could not be found in the geometry optimization of 2-mercaptobezaldehyde even with basis sets much larger than 6-31G*.

TABLE 1: Geometrical Parameters for Salicylaldehyde 1a at Various Levels of Calculation (Distances, Å; Angles, deg)

parameters	RHF 6-31G**	RHF 6-31+G*	RHF 6-311G*	B3LYP 6-31G**	B3LYP 6-31+G*	B3LYP 6-311G*	MP2 6-31G*[a]	exptl value[a]
C_1-C_2	1.399	1.400	1.398	1.409	1.411	1.407	1.406	
C_1-C_3	1.402	1.403	1.401	1.422	1.422	1.419	1.414	1.418(14)
C_2-C_5	1.373	1.375	1.373	1.384	1.386	1.382	1.387	
C_3-C_6	1.394	1.395	1.394	1.403	1.404	1.401	1.401	
C_5-C_{11}	1.395	1.397	1.395	1.406	1.407	1.403	1.403	
C_6-C_{11}	1.376	1.378	1.375	1.389	1.390	1.385	1.390	
C_1-C_4	1.464	1.465	1.466	1.453	1.454	1.454	1.460	1.462(11)
C_3-O_8	1.328	1.331	1.328	1.341	1.344	1.341	1.353	1.362(10)
C_4-O_7	1.201	1.203	1.195	1.234	1.236	1.227	1.240	1.225(4)
C_4-H_9	1.094	1.092	1.093	1.108	1.107	1.107	1.106	1.11(5)
O_8-H_{12}	0.952	0.956	0.946	0.991	0.990	0.981	0.989	0.985(14)
O_7---H_{12}	1.882	1.896	1.906	1.822	1.779	1.792	1.803	1.74(2)
O_7---O_8	2.693	2.703	2.709	2.675	2.563	2.655	2.681	2.65(1)
$\angle C_1C_2C_5$	121.33	121.38	121.39	120.96	120.95	121.06	120.67	121.5(29)
$\angle C_1C_3C_6$	119.36	119.44	119.32	119.34	119.45	119.25	119.28	120.9(9)
$\angle C_2C_1C_3$	119.34	119.29	119.33	119.45	119.36	119.38	119.74	118.2(18)
$\angle C_2C_5C_{11}$	118.56	118.55	118.54	119.00	119.02	118.93	119.19	119.0(12)
$\angle C_5C_{11}C_6$	121.49	121.40	121.41	121.45	121.39	121.38	121.05	121.5(8)
$\angle C_3C_6C_{11}$	119.92	119.94	120.02	119.81	119.83	120.00	120.06	118.9(19)
$\angle C_3C_1C_4$	121.20	121.45	121.34	121.16	120.35	120.55	120.80	121.4(8)
$\angle C_1C_3O_8$	122.80	122.91	123.13	121.89	121.96	122.21	122.72	120.9(11)
$\angle C_1C_4O_7$	124.90	124.80	125.09	124.60	124.46	124.76	124.54	123.8(12)
$\angle O_7C_4H_9$	119.73	119.56	119.56	119.39	119.33	119.32	119.38	119.7(34)
$\angle C_1C_4H_9$	115.37	115.62	115.35	116.02	116.22	115.93		116.5(37)
$\angle C_3O_8H_{12}$	110.28	110.67	110.14	110.17	108.10	108.27	106.97	104.8(26)

[a] Reference 19.

The optimized geometrical parameters for conformer **1a** of salicylaldehyde at the various levels of theory are listed in Table 1 along with the experimental values[19] and the results of the previous MP2 study.[19] Although overall computed geometrical parameters at the RHF levels are well matched with the experimental ones, the computed parameters related to the CHO and OH substituents, such as C_3-O_9, C_4-O_7, O_8-H_{13} bond lengths and bond angle $\angle C_3O_8H_{12}$, noticeably deviate from the experimental ones. These discrepancies considerably reduce by taking into account the electron correlation effect at the B3LYP levels. For the benzene ring geometry, the C_1-C_3 bond length between two substituents somewhat lengthens as the effect of electron correlation is taken into account. Among C−C bond lengths in the benzene ring, C_2-C_5 and C_6-C_{11} bond lengths are somewhat longer than others. This feature is well rationalized with the resonance structure of this molecule.

The C_3-O_9 bond length is computed to be about 1.34 Å at the B3LYP/6-311G* level, which is about 0.01 and 0.02 Å shorter than MP2 and experimental values, respectively. Both C_4-O_7 and O_8-H_{13} bond lengths computed at the B3LYP/6-311G* level are in excellent agreement with experimental ones. On the other hand, the bond angle $\angle C_3O_8H_{12}$ around the hydroxyl oxygen shows a somewhat peculiar aspect of a decrease of the bond angle when the electron correlation is taken into account at the B3LYP levels. At the B3LYP/6-311G* level, this bond angle is computed to be 108.27°, which is about 3° larger than the experimental value of 104.8(26)°. Considering the experimental uncertainty, this difference is not so serious as to understand the nature of this bond angle. The MP2 result can be used to judge the accuracy of this computed value. From the previous study,[19] this bond angle is computed to be 106.97° at the MP2/6-31G* level, which is not much different from our B3LYP/6-311G* result. This fact justifies that geometrical parameters computed at the B3LYP levels are well consistent with experimental values.

The hydrogen bond distances change sensitively not only by adding the electron correlation effect but also by increasing the size of basis set. The O_7---H_{12} distance in conformer **1a** is computed to be 1.792 Å at the B3LYP/6-311G* level, which is in good agreement with that of the previous MP2 value of 1.803 Å, even though this value is about 0.05 Å larger than the experimental value of 1.74(2) Å. The computed distance O_7---O_8 between two neighboring oxygen atoms is another example to convince the accuracy of our DFT result. This computed value of 2.655 Å at the B3LYP/6-311G* level is much closer to the experimental value of 2.65(1) Å than that of the previous MP2 results.

The optimized geometrical parameters for the most stable conformer **2a** of 2-mercaptobenzaldehyde at various ab initio and B3LYP levels are summarized in Table 2. As can be seen in this table, overall structural parameters at the MP2 level are in good agreement with those calculated at the B3LYP levels. In this molecule, the optimized parameters around two adjacent substituents—CHO and SH—also change sensitively by adding the electron correlation effect at both B3LYP and MP2 levels. This trend is very similar to the variation of geometrical parameters around two adjacent substituents—CHO and OH—in salicylaldehyde **1a**. However, the C_3-S_8 bond lengths at the RHF levels are almost the same as those at the B3LYP levels. On the other hand, the bond angle $\angle C_3S_8H_{12}$ is computed to be 95.3° at the B3LYP/6-311G* level, which is about 3° less than that at the RHF levels. This similar sort of the bond angle reduction is not only found in its oxygen analogue, that is, salicylaldehyde **1a**, but also discussed in the theoretical studies for other intramolecular hydrogen-bonding systems such as 2-nitroresorcinol[1,2] and 4,6-dinitroresorcinol.[3]

From the results of theoretical studies for salicylaldehyde and other intramolecular hydrogen-bonding systems,[1−3] it is found that adding the electron correlation effect produces the reduction of the bond angle ∠COH in the hydrogen donor hydroxyl group, and the computed bond angles at the MP2 or B3LYP levels are in general much closer to the experimental value than those at the RHF levels. In the geometry of the benzene ring of 2-mercaptobenzaldehyde, the shortening of two bond lengths such as C_2-C_5 and C_6-C_{11} appears just as discussed in salicylaldehyde. The hydrogen bond distance O_7---H_{12} of 2-mercaptobenzaldehyde is computed to be 1.932 Å at the MP2/6-31G* level, which is about 0.03 Å longer than that at the

TABLE 2: Geometrical Parameters for 2-Mercaptobenzaldehyde 2a at Various Levels of Calculation (Distances, Å; Angles, deg)

parameters	RHF 6-31G**	RHF 6-31+G*	RHF 6-311G*	B3LYP 6-31G**	B3LYP 6-31+G*	B3LYP 6-311G*	MP2 6-31G*
C_1-C_2	1.397	1.398	1.396	1.410	1.412	1.408	1.408
C_1-C_3	1.403	1.405	1.403	1.420	1.422	1.418	1.416
C_2-C_5	1.377	1.379	1.376	1.386	1.388	1.383	1.388
C_3-C_6	1.393	1.395	1.392	1.405	1.407	1.402	1.404
C_5-C_{11}	1.387	1.388	1.386	1.400	1.402	1.397	1.399
C_6-C_{11}	1.380	1.382	1.380	1.390	1.391	1.387	1.391
C_1-C_4	1.481	1.482	1.483	1.471	1.470	1.471	1.475
C_3-S_8	1.774	1.773	1.773	1.772	1.770	1.773	1.767
C_4-O_7	1.193	1.194	1.187	1.225	1.227	1.218	1.233
C_4-H_9	1.095	1.093	1.094	1.110	1.109	1.109	1.108
S_8-H_{12}	1.321	1.321	1.323	1.356	1.355	1.357	1.343
O_7---H_{12}	2.045	2.057	2.065	1.880	1.904	1.901	1.932
O_7---S_8	3.115	3.121	3.127	3.059	3.071	3.072	3.088
$\angle C_1C_2C_5$	122.03	122.05	122.09	121.88	121.93	121.91	121.59
$\angle C_1C_3C_6$	118.55	118.52	118.54	118.51	118.51	118.60	118.12
$\angle C_2C_1C_3$	119.03	119.05	119.00	119.02	118.98	118.90	119.50
$\angle C_2C_5C_{11}$	118.56	118.52	118.54	118.74	118.67	118.77	118.89
$\angle C_5C_{11}C_6$	120.57	120.55	120.50	120.62	120.68	120.60	120.30
$\angle C_3C_6C_{11}$	121.26	121.32	121.35	121.23	121.24	121.22	121.60
$\angle C_3C_1C_4$	125.67	125.75	125.74	125.18	125.34	125.27	125.40
$\angle C_1C_3S_8$	126.58	126.73	126.77	124.91	125.21	125.25	125.93
$\angle C_1C_4O_7$	127.35	127.33	127.53	127.53	127.39	127.63	127.24
$\angle O_7C_4H_9$	119.36	119.26	119.26	118.99	118.83	118.89	119.10
$\angle C_1C_4H_9$	113.29	113.51	113.22	113.48	113.78	113.48	113.66
$\angle C_3S_8H_{12}$	98.63	98.86	98.96	95.04	95.62	95.30	95.43

B3LYP levels. It has been reported that the DFT calculations sometimes give less reliable results for weakly bonded systems such as the hydrogen-bonding molecules[27,28] and van der Waals complexes.[29] According to previous studies,[27,28] hydrogen bond distances for several complexes computed at the B3LYP levels with medium-sized basis sets are somewhat shorter than those computed at the MP2 level as well as experimental values. Therefore, one can imagine that the O_7---H_{12} distances at the B3LYP levels might be a little less reliable than the MP2 result. The computed distance O_7---S_8 between oxygen and sulfur atoms at the MP2 level is 3.088 Å, which is approximately at the midpoint between the values at the RHF and B3LYP levels.

The structural difference between salicylaldehyde and 2-mercaptobenzaldehyde can be one of the clues to understand how much different the hydrogen bonding between these two molecules is. In comparison of bond lengths in the benzene ring, the serious differences between two analogues are not found. However, the noticeable differences of bond lengths in the CHO group are seen at a glance. The computed C_1-C_4 bond length of salicylaldehyde at the B3LYP/6-311G* level is about 0.02 Å shorter than that of 2-mercaptobenzaldehyde, while the C_4-O_7 bond length shows the reverse trend. From the resonance structures, C_1-C_4 and C_4-O_7 bonds show some double- and single-bond character, respectively. It can be suggested that these two bonds of 2-mercaptobenzaldehyde are much less affected by resonance than those of salicylaldehyde.

On the other hand, the bond angles of 2-mercaptobenzaldehyde such as $\angle C_3C_1C_4$, $\angle C_1C_3S_8$, and $\angle C_1C_4O_7$ at both RHF and B3LYP levels are much larger than those of its oxygen analogue. The differences of these endocyclic angles in a six-membered ring formed by both two substituents between these two analogues may be caused by the charge difference between O−H and S−H groups. Hence, two substituents in 2-mercaptobenzaldehyde are more tilted away from each other than those in salicylaldehyde, so that the hydrogen bond distance for salicylaldehyde computed at the B3LYP/6-311G* level is about 0.1 Å shorter than that for its sulfur analogue. Therefore, it can be concluded that the O---H interaction in salicylaldehyde is somewhat stronger than that in 2-mercaptobenzaldehyde if one disregards other factors such as the difference of the bonding environments between O−H and S−H functional groups.

Dependence of the Molecular Structure upon the Conformation. To know how much a molecular structure is affected by hydrogen bonding, it is necessary to discuss the dependence of geometrical parameters upon a change of conformation. The differences of computed geometrical parameters between two neighboring conformers (see Figures 1 and 2) among four possible conformers of both salicylaldehyde and 2-mercaptobenzaldehyde at the B3LYP/6-311G* level are summarized in Table 3.

As can be seen in Table 3, overall bond length deviations for each conformer of salicylaldehyde are much more sensitive than those for each conformer of 2-mercaptobenzaldehyde. This trend is particularly evident in a change of conformation between conformers **1a** and **1b** in salicylaldehyde. When hydrogen bonding O_7---H_{12} is prevented by the rotation of the hydroxyl group in conformer **1b**, O_8-H_{12}, C_4-O_7, and C_3-O_8 bond lengths are somewhat altered, while their equivalent bonds in conformer **2b** are almost unchanged. However, the characteristic feature between two analogues can be seen in a considerable change of bond angles when the hydroxyl group of the most stable conformer is rotated up to 180° in order to prevent hydrogen bonding. Bond angles of conformer **1b** such as $\angle C_3O_8H_{12}$, $\angle C_1C_4O_7$, and $\angle C_3C_1C_4$ increase by about a few degrees compared to those of conformer **1a**, while its equivalent bond angles of conformer **2b** decrease by about the same amount of degrees. These differences may be ascribed to the opposite behavior between O_7---O_8 and O_7---S_8 interactions. According to the natural population analyses, the computed net charges of oxygen and sulfur atoms in 2-mercaptobenzaldehyde have signs opposite to each other, while those of two oxygen atoms in salicylaldehyde have the same negative charges. Therefore, one can expect that there is strong Coulombic attraction between sulfur and oxygen atoms. The computed O_7---O_8 and O_7---S_8 distances of salicylaldehyde and 2-mercaptobenzaldehyde, respectively, well support this expectation. The O_7---O_8 distance of conformer **1b** is computed to be 2.783 Å at the B3LYP/6-311G* level, which is about 0.1 Å larger than that of conformer

TABLE 3: Differences of Selected Geometrical Parameters among Possible Conformers of Salicylaldehyde and 2-Mercaptobenzaldehyde at the B3LYP/6-311G* (Distances, Å; Angles, deg)

	salicylaldehyde			2-mercaptobenzaldehyde		
parameters	Δ(**1b**−**1a**)	Δ(**1c**−**1b**)	Δ(**1d**−**1c**)	Δ(**2b**−**2a**)	Δ(**2c**−**2b**)	Δ(**2d**−**2c**)
C_1-C_3	−0.005	−0.006	0.004	−0.003	−0.005	0.004
O_8-H_{12}	−0.016	−0.001	−0.002			
S_8-H_{12}				−0.001	−0.006	0.001
C_4-O_7	−0.020	0.005	−0.001	−0.006	−0.001	0.010
C_3-O_8	0.012	0.011	−0.002			
C_3-S_8				0.005	0.013	0.011
C_4-H_9	0.008	−0.010	0.012	0.002	−0.003	−0.004
$\angle C_3O_8H_{12}$	1.16	0.47	1.39			
$\angle C_3S_8H_{12}$				−1.54	1.71	2.51
$\angle C_1C_4O_7$	2.78	−3.79	1.51	−2.42	−0.98	−0.32
$\angle C_3C_1C_4$	3.50	−2.49	1.16	−2.98	0.22	0.30
$\angle C_1C_3O_8$	−3.21	−0.90	6.31			
$\angle C_1C_3S_8$				−4.66	−0.26	3.68

1a. On the contrary, the O_7---S_8 distance of conformer **2b** is about 0.3 Å shorter than that of conformer **2a**.

When the hydrogen atom of the CHO group faces the oxygen atom of the O−H group in conformer **1c**, the C_3-O_8 bond length somewhat increases, while the C_4-H_9 bond length decreases. However, it can be seen from Δ(**2c-2b**) in Table 3 that the C_3-S_8 bond length somewhat increases while the C_4-H_9 bond length of conformer **2c** rarely changes by the rotation of CHO group. In addition, variations of bond angles of conformer **2c** are also less than those of bond angles of conformer **1c**. When the hydroxyl group of conformer **1c** is further rotated by 180°, both hydrogen atoms of two substituents face each other in conformer **1d**. In this course of a change of conformation, the most apparent structural change is at the bond angle $\angle C_1-C_3-O_8$. The computed difference of this bond angle between conformers **1d** and **1c** is approximately 6°. This result strongly suggests that there is a considerable repulsion between two substituents in conformer **1d**. The computed H_9---H_{12} distance in conformer **1d** at the B3LYP/6-311G* level is 1.888 Å, which is quite shorter than the twice the van der Waals radius of the hydrogen atom. Therefore, this nonbonding interaction makes the hydroxyl group tilt away from the CHO group to some degree.

On the other hand, the differences of computed geometrical parameters between conformers **2d** and **2c** in 2-mercaptobenzaldehyde quite differ from those of computed parameters between conformers **1d** and **1c** in salicylaldehyde. Bond angles such as $\angle C_3S_8H_{12}$ and $\angle C_1C_3S_8$ increase by about 3° as the conformation is changed from **2c** to **2d**.

^{1}H Chemical Shift of 2-Mercaptobenzaldehyde. In this section, we predict the predominant conformation of 2-mercaptobenzaldehyde by ^{1}H NMR chemical shifts because there are no experimental structures reported for this molecule up to date. Table 4 summarizes the computed ^{1}H NMR chemical shifts (ppm) for 2-mercaptobenzaldehyde both at the RHF/6-31+G*//B3LYP/6-31+G* and B3LYP/6-31+G*//B3LYP/6-31+G* levels along with its experimental values.[18] As can be seen in Table 4, the computed chemical shifts at both RHF and B3LYP levels are not much different. The calculated chemical shifts for conformer **2a** are in better agreement with experimental values than those for the other three conformers. The most noticeable difference of chemical shifts between theory and experiment is of the S−H proton (H_{12}). In conformer **2a**, this value is computed to be about 7.3 ppm at the B3LYP/6-31+G* level, which deviates from the experimental value by about 1 ppm. However, the computed chemical shifts of this proton for the other three conformers are about 3 ppm. This value is significantly different from the experimental value of 6.2 ppm. Therefore, one can infer that conformer **2a** is really predominant in this compound.

TABLE 4: ^{1}H NMR Chemical Shifts (in ppm) of Possible Conformers for 2-Mercaptobenzaldehyde at the B3LYP/6-31+G* Optimized Geometry[a]

		2a		**2b**		**2c**		**2d**	
atoms	exptl[b] value	I[c]	II[d]	I	II	I	II	I	II
H_9	9.98	9.46	9.91	9.64	10.08	9.92	10.42	10.53	10.55
H_{12}	6.21	7.64	7.30	3.11	3.49	3.07	3.15	3.35	3.23
H_{10}	7.63	7.43	7.30	7.60	7.45	8.42	8.03	8.82	8.07
H_{13}	7.21	6.81	7.05	6.94	7.08	6.93	7.02	7.31	7.31
H_{14}	7.25	7.12	7.24	6.87	6.97	6.68	6.80	7.85	7.51
H_{15}	7.31	7.35	7.25	7.32	7.18	7.30	7.16	7.86	7.40

[a] Relative to tetramethylsilane. [b] Reference 18. [c] RHF/6-31+G*//B3LYP/6-31+G*. [d] B3LYP/6-31+G*//B3LYP/6-31+G*.

On the other hand, the aldehyde protons (H_9) in both conformers **2c** and **2d** are about 0.5 ppm more shielded than those in conformers **2a** and **2b**. This may be ascribed to the weak interaction between sulfur and hydrogen atoms. Similarly, the result that the protons H_{10} in both conformer **2c** and **2d** show much larger chemical shift than those in conformers **2a** and **2b** can be also interpreted by the same effect, that is, the existence of the weak interaction between O_7 and H_{10} atoms. In comparison between conformers **2c** and **2d**, the chemical shift of the proton H_{14} on the benzene ring in conformer **2d** is computed to be 7.85 ppm at the HF/6-31+G* level, which is about 1.2 ppm larger than that in conformer **2c**. This fact may be well related with the interaction between the 3p orbital of the sulfur atom and this proton. In other words, the directional $3p_y$ orbital lying in the same plane as the benzene ring, which is caused by torsion of the S−H group by about 90° in conformer **2d,** can interact with the proton H_{14} as well as the S−H proton. This assumption can be justified from the result that the chemical shift of this proton somewhat decreases at the B3LYP/6-31+G* level. From the results of our geometry optimization, the perpendicularlity of the S−H group of conformer **2d** decreases as the electron correlation effect is taken into account at the B3LYP levels.

Relative Energy among Possible Conformers. The relative energies (kcal/mol) at various RHF and B3LYP levels for several possible conformers of salicylaldehyde and 2-mercaptobenzaldehyde are listed in Table 5. In the results of salicylaldehyde, the computed energy differences between conformers **1a** and **1b** are approximately 10 and 12 kcal/mol at both RHF and B3LYP levels, respectively. The intramolecular hydrogen-bonding energy can be estimated by comparing the relative energy between a conformer with hydrogen bond and

TABLE 5: Relative Energies (kcal/mol)for Salicylaldehyde and 2-Mercaptobenzaldehyde Conformers at Various Levels of Calculation

	1a	1b	1c	1d	2a	2b	2c	2d
RHF/6-31G**	0.00	10.42	6.13	9.00	0.00	1.23	1.22	1.00
RHF/6-31+G*	0.00	10.18	5.95	8.88	0.00	1.30	1.18	0.91
RHF/6-311G*	0.00	10.02	5.62	8.55	0.00	1.10	1.14	0.36
B3LYP/6-31G**	0.00	12.18	9.39	10.72	0.00	1.80	3.76	4.81
B3LYP/6-31+G*	0.00	11.47	8.66	10.10	0.00	1.78	3.32	4.31
B3LYP/6-311G*	0.00	11.65	8.52	10.02	0.00	1.53	3.49	4.24

another possible conformer with no hydrogen bond. In previous theoretical studies,[30,31] either conformer **1b** or **1c** is suggested to estimate the hydrogen-bonding energy of salicylaldehyde as the reference conformer. However, a recent theoretical study[18] shows that conformer **1c** is found to be the genuine reference conformer. Therefore we may suggest that the relative energy of conformer **1c** with respect to conformer **1a** is the hydrogen-bonding energy of salicylaldehyde, which is computed to be 8.52 kcal/mol at the B3LYP/6-311G* level. This value is in good agreement with the experimental value of 7.9 kcal/mol.[1]

On the other hand, the energy difference between conformers **1b** and **1d** is computed to be about 1.5 kcal/mol at both RHF and B3LYP levels. Of course, such a little difference in energy is not enough to determine the stability of a conformer. However, this fact suggests that the Coulombic interaction is more important to determine the stability of a conformer than the van der Waals interaction. More precisely, the H_9---H_{12} distance of conformer **1d** is computed to be 1.888 Å at the B3LYP/6-311G* level, which is about 0.5 Å shorter than twice the van der Waals radius of the hydrogen atom. In conformer **1b**, the computed O_7---O_8 distance is about 0.2 Å shorter than twice the van der Waals radius of the oxygen atom. Therefore, one can infer that conformer **1d** is more unstable than conformer **1b**. Nevertheless, both conformers **1b** and **1d** show almost equal stability. It may be because the Coulombic repulsion between two large negative-charged oxygen atoms in conformer **1b** is more important to account for the relative stability of this conformer than the van der Waals repulsion.

The relative energies among possible conformers of 2-mercaptobenzaldehyde give us somewhat different features from those of salicylaldehyde. First of all, the hydrogen-bonding energy estimated by comparing the energy between the two conformers **2a** and **2b** is considerably lower than that of its oxygen analogues in salicylaldehyde. This value is computed to be less than 2 kcal/mol at both RHF and B3LYP levels. From the result of previous theoretical study,[18] the characteristic stability of conformer **2b** may be ascribed to the Coulombic attraction between the negative-charged oxygen and positive-charged sulfur atoms. In addition, three conformations, **2b**, **2c**, and **2d**, are almost isoenergetic at the RHF levels of calculation. However, this situation is somewhat altered by adding the electron correlation effect at the B3LYP levels. B3LYP calculations show that the relative stability of these three conformers is in order **2b** > **2c** > **2d**. Especially, the electron correlation effect at the B3LYP levels makes the energy difference between conformers **2d** and **2a** sensitively increased. This variation of the relative stability of conformer **2d** may be strongly related to the perpendicularity of the S−H group in the B3LYP calculations, which is discussed above.

The previous study[18] had also concluded that either conformer **2b** or **2c** could make the reference conformer for estimating the intramolecular hydrogen-bonding energy of 2-mercaptobenzaldehyde. However, we suggest that conformer **2b** would be the genuine reference conformer since there is about 2 kcal/mol difference in energy between these two conformers at the B3LYP levels of calculation. Therefore, the estimated hydrogen-bonding energy of 2-mercaptobenzaldehyde is 1.53 kcal/mol at the B3LYP/6-311G* level. This amount of energy is only one-fifth of the hydrogen-bonding energy of salicylaldehyde.

In addition, we also compare the energy difference between two conformers of salicylthioaldehyde (2-hydroxybenzenecarbothioaldehyde) in which O_7 and S_8 atoms in both conformers **2a** and **2b** are exchanged each other. The energy difference between these two conformers is computed to be about 11 kcal/mol at the B3LYP/6-31G** level. This magnitude is much the same as the energy difference between **1a** and **1b** of salicylaldehyde (∼12 kcal/mol) at the B3LYP levels. Although this value is considerably larger than that of 2-mercaptobenzaldehyde, it is not surprising since both oxygen and sulfur atoms have the same negative charges as in salicylaldehyde. This result well supports that the Coulombic attraction between oppositely charged S and O atoms in conformer **2b** plays an important role in stabilizing this conformer.

Conclusion

The molecular structures and the nature of intramolecular hydrogen bonding for both salicylaldehyde and 2-mercaptobenzaldehyde are theoretically investigated with an ab initio method as well as the density functional theory. In salicylaldehyde, the computed geometrical parameters of conformer **1a** at the B3LYP levels are in better agreement with experimental values than those at the RHF levels. Some geometrical parameters such as the bond angle $\angle C_3O_8H_{12}$ and hydrogen bond distance O_7---H_{12} in particular at the B3LYP levels are much closer to the experimental one than those at the RHF levels. In 2-mercaptobenzaldehyde, the overall computed molecular parameters of conformer **2a**, except for geometrical parameters involving two substituents, are not much different from those of its oxygen analogue—salicylaldehyde **1a**. Overall computed geometrical parameters for this molecule at the B3LYP levels are in good agreement with the MP2 result. However, the computed hydrogen bond distance at the B3LYP levels is somewhat shorter than that at the MP2 level.

Careful conformational analyses of given molecules show that both the size and charge differences between oxygen and sulfur atoms in these two analogues are very important factors not only for comparing their conformational behaviors but also for understanding the nature of hydrogen bonding. On the other hand, the existence of the π-type hydrogen bonding between the 1s orbital of the hydrogen atom and the 3p orbital of the sulfur atom in 2-mercaptobezaldehyde **2d** is not evident. In addition, the computed ^{1}H NMR chemical shifts for conformer **2a** of 2-mercaptobenzaldehyde at the B3LYP/6-31+G*//B3LYP/6-31+G* level, which are well matched with experiments, support the conformational behavior of this molecule as well.

The energy of intramolecular hydrogen bonding is estimated by making a comparison of molecular energies between two different conformations. In salicylaldehyde, the hydrogen bond energy of about 8.5 kcal/mol at the B3LYP/6-311G* level is in good agreement with the previous experimental value of 7.9 kcal/mol. In 2-mercaptobenzaldehyde, we suggest that the hydrogen-bonding energy is about 1.5 kcal/mol by the energy difference between conformers **2a** and **2b**. The difference of Coulombic interaction between O---O and O---S in these two analogues might be one of the reasons that the hydrogen-bonding energy for 2-mercaptobenzaldehyde is much weaker than that for its oxygen analogue—salicylaldehyde.

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