Theoretical Study on 1,2-Dihydroxybenzene and 2-Hydroxythiophenol: Intramolecular Hydrogen Bonding

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The molecular structures and the intramolecular hydrogen bonding for 1,2-dihydroxybenzene and 2-hydroxythiophenol have been precisely investigated by an ab initio method and density functional theory (DFT). We have considered the several possible conformations with different types of intramolecular hydrogen bonding in given molecules to understand the nature of the hydrogen bonding among these conformers. The optimized geometrical parameters for conformer **1a** at the B3LYP levels as well as the computed ^{1}H NMR chemical shifts for conformer **2b** at the RHF/6-31+G*//B3LYP/6-31+G* level are in good agreement with previous experimental results. It is confirmed from these results that the inclusion of electron correlation is crucial to elucidate molecular properties for the intramolecular hydrogen bonding systems. We have also compared the molecular energies between two different conformations both with a hydrogen bond and with no hydrogen bond of a given molecule. In 1,2-dihydroxybenzene, the energy stabilized by hydrogen bonding is about 4 kcal/mol at both ab initio and DFT methods. However, the hydrogen bonding energies are different according to types of hydrogen bonding in 2-hydroxythiophenol: about 1 kcal/mol for conformer **2a** with the common type hydrogen bonding and 4 kcal/mol for conformer **2b** with the π type hydrogen bonding.

Introduction

Hydrogen bonding has been a very important research area for chemists for a long time since it can account for characteristics of many chemical and biological phenomena. The informations on intramolecular hydrogen bonding in particular are very useful to understand various molecular properties. The intramolecular hydrogen bonding can be sometimes very responsible for the molecular geometries as well as the stability of a certain predominant conformation. Since the rapid development of computer hardware and software algorithms makes possible theoretical approaches to a wide variety of molecular systems, many investigations of intramolecular hydrogen bonding in terms of molecular orbitals have recently been performed not only by semiempirical methods [1,2] but also by ab initio methods.[3−11]

Among many molecular properties that are affected by intramolecular hydrogen bonding, the molecular structure of a predominant conformation has been widely investigated not only by theoretical approaches but also by experimental methods. In such aspect, some molecular orbital studies on ortho-substituted phenol derivatives such as 2-nitrophenol,[7] 2-nitroresorcinol,[8,9] 4,6-dinitroresorcinol,[10] and salicylaldehyde[11,12] have been performed. In particular, 2-hydroxythiophenol[13,14] and its derivatives[15−18] have recently become attractive to theoreticians as well as experimentalists since they have a new type of intramolecular interaction called the π type hydrogen bond.[13,14] For example, among several conformers of 2-hydroxythiophenol, three of them make up different types of intramolecular hydrogen bonding: two of them are of the common type with either S···H or O···H hydrogen bond and the third one is of the π type S···H hydrogen bond. An IR study[15] shows that two conformers with the common hydrogen bond exist in an equal ratio of concentrations. However, the previous NMR experiment [13] shows that there is a strong evidence for the predominance of the intramolecular π type hydrogen bond in which the S−H group prefers to lie perpendicular to the benzene plane. Some theoretical studies on 2-hydroxythiophenol[13] and its derivatives[16] were also performed previously by both semiempirical and ab initio methods with minimal basis sets. However, more precise investigations at higher levels of theory are still demanded since these previous theoretical studies could not perfectly explain the nature of intramolecular hydrogen bonds and conformational behavior of these molecules.

In this article, we are going to investigate both molecular structures and characteristics of intramolecular hydrogen bonds for 1,2-dihydroxybenzene and 2-hydroxythiophenol in terms of molecular orbitals by an ab initio method as well as the density functional theory (DFT). DFT has been shown to be successful in predicting various molecular properties, often giving results of a quality comparable or even better than MP2[19−21] for a cost that is substantially less than that of traditional correlation techniques. On the other hand, DFT has become in recent years a promising alternative to conventional ab initio methods in quantum chemistry. It therefore seems reasonable to investigate in detail how well DFT predicts equilibrium geometries for molecules containing intramolecular hydrogen bonding in particular since the incorporation of electron correlation is required to describe molecular properties of such hydrogen bonding molecules.[22,23] The results of previous studies[23−26] indicate that the calculated molecular properties with the DFT methods are in excellent agreement with available experimental data in benzene analogues as well as systems containing hydrogen bonds. We compare the optimized geometrical parameters of hydrogen bonding conformers with two different types and discuss their bonding properties by using natural population analysis(NPA).[27] We also calculate ^{1}H NMR chemical shifts for 2-hydroxythiophenol to compare with experimental values.[13] Finally, we estimate the hydrogen

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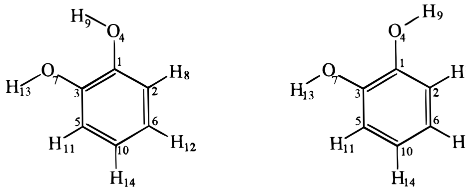


1a **1b**

Figure 1. Possible conformers of 1,2-dihydroxybenzene (**1a**, syn−anti form; **1b**, anti−anti form).

bonding energies for different conformers in these two molecules at the various levels of theory.

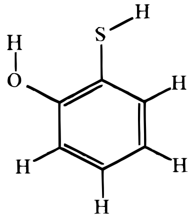
Computational Details

The molecular geometries of possible conformers for 1,2-dihydroxybenzene and 2-hydroxythiophenol are fully optimized at the various levels of theory using the Gaussian 94 program [28] without any geometrical restrictions. We have carried out the geometry optimization first at the restricted Hartree−Fock (RHF) levels by using 6-31G**, 6-31+G*, 6-311G*, and 6-311+G* 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[29−31] in the density functional theory with 6-31G**, 6-31+G*, and 6-311G* basis sets. The reason is that the B3LYP method provides energetics typically better than the Hartree−Fock (HF) method[30] and can reproduce better geometrical parameters comparable to the experimental values than any other methods.[32] In addition, the B3LYP results are closer to correlated post-Hartree−Fock approximations such as the MP2 method or better.[19,20] 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 2-Hydroxythiophenol and 1,2-Dihydroxybenzene. Molecular geometries of possible conformers for 1,2-dihydroxybenzene are shown in Figure 1 along with the numbering of atoms. Two conformers are termed as the syn−anti conformer **1a** with a single hydrogen bond, and the anti−anti conformer **1b** with no hydrogen bonding according to the positions of two neighboring O−H groups. The optimized geometrical parameters for conformer **1a** of 1,2-dihydroxybenzene at the various RHF and B3LYP levels are summarized in Table 1 along with experimental values.[33] The overall computed geometrical parameters at both the RHF and B3LYP levels are in good agreement with experimental values. In the RHF calculations, all geometrical parameters for conformer **1a** of 1,2-dihydroxybenzene have hardly changed despite an increase of the size of the basis set. However, they have somewhat changed as the electron correlation effects are included at the B3LYP levels. These results ensure that the basis set effects on the computed geometry at the post Hartree−Fock levels are much more important than those at the RHF levels.[34] The geometrical parameters around two O−H groups in particular are of much more interest than other values. Both O_4-H_9 and O_7-H_{13} bond lengths are computed to be about 0.97 Å at the B3LYP levels, which are much closer to experimental values than those from RHF calculations. The $C_1-O_4-H_9$ bond angle around the hydrogen donor O−H group decreases sensitively as the electron correlation effects are taken into account. This value is computed to be 108.11° at the B3LYP/6-311G* level, which is in excellent agreement with experimental value of 108.28°. The $C_3-O_7-H_{13}$ bond angle around the hydrogen acceptor O−H group is less sensitive to change with respect to the electron correlation than the $C_1-O_4-H_9$ bond angle of the hydrogen donor O−H group.

Molecular geometries of possible conformers for 2-hydroxythiophenol are shown in Figure 2. Three conformers for this molecule are subdivided into the syn-anti conformer **2a** with a single O···H hydrogen bond, the syn−gauche conformer **2b** with a single S···H hydrogen bond, and the anti−anti conformer **2c** with no hydrogen bond. In conformer **2b** there exists the OH···3p(S) hydrogen bond in which the directional lone pair 3p orbital on sulfur is twisted into the benzene plane by electrostatic forces from the polar O−H bond. Consequently, the S−H bond is now in the plane otherwise occupied by the 3p electron pair. Thus, the S−H group lies almost perpendicular to the benzene plane. Three conformers differ only in the spatial direction of both O−H and S−H groups. In addition, the possibility of the existence of another conformer **2d** which has C_s symmetry with a common type of a single hydrogen bond between sulfur and hydrogen atoms was reported with the semiempirical CNDO/2 calculations.[13] However, the local minimum of this conformation could not be found in the geometry optimization at both the RHF and B3LYP levels even with much larger basis sets than 6-31G**.



2d

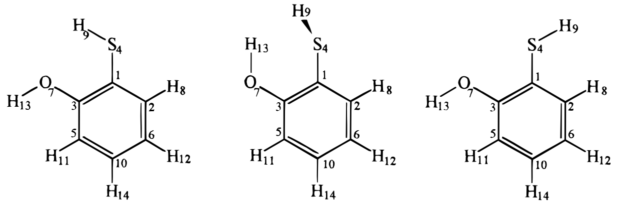
The optimized geometrical parameters for the most stable conformers **2b** and another possible conformer **2a** of 2-hydroxythiophenol at various RHF and B3LYP levels are listed in Tables 2 and 3, respectively. Geometry optimizations at both RHF and B3LYP levels show that both conformers **1a** and **1b** of 1,2-dihydroxybenzene might have C_s symmetry since the deviations of torsional angles for two O−H groups from the plane of benzene ring in conformers **1a** and **1b** are less than 0.01°. On the other hand, optimized geometries of conformer **2a** of 2-hydroxythiophenol at the RHF levels show that the S−H group is not located in the same plane of the benzene ring, while conformer **2c** with no hydrogen bonding has a plane of symmetry. However, the torsional angle of the S−H group in conformer **2a** at the B3LYP levels becomes around 0°. The torsional angle of the S−H group in conformer **2b** in particular is computed to be about 90° at both RHF and B3LYP theoretical levels. This supports that the S−H group in conformer **2b** lies almost perpendicular to the plane of the benzene ring.

In RHF calculations, all geometrical parameters for both conformers **2a** and **2b** of 2-hydroxythiophenol have not changed very much despite an increase of the size of the basis set. When the electron correlation is seriously taken into account at the B3LYP levels, geometrical parameters of all conformers are generally somewhat altered. Some geometrical parameters connected with specific atoms which are involved in intramolecular hydrogen bonding such as S−H, O−H, and C−O bonds are much sensitive to variation with respect to basis sets. In conformer **2b**, the bond lengths in particular such as C_1-S_4, C_3-O_7, S_4-H_9, and O_7-H_{13} at the B3LYP levels are about 0.02 Å larger than those from RHF calculations. However, the inclusion of electron correlation does not affect the bond length

TABLE 1: Geometrical Parameters for 1,2-Dihydroxybenzene, 1a, at RHF and B3LYP Levels (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*	exptl[a]
C_1-C_2	1.379	1.381	1.378	1.392	1.393	1.389	
C_1-C_3	1.392	1.392	1.392	1.405	1.404	1.404	1.397
C_2-C_6	1.389	1.390	1.388	1.398	1.399	1.396	
C_3-C_5	1.378	1.380	1.377	1.391	1.392	1.388	
C_5-C_{10}	1.390	1.391	1.389	1.399	1.400	1.396	
C_6-C_{10}	1.381	1.384	1.380	1.394	1.396	1.391	
C_1-O_4	1.350	1.350	1.348	1.365	1.366	1.362	1.323
C_3-O_7	1.364	1.363	1.362	1.380	1.382	1.378	1.406
O_4-H_9	0.950	0.949	0.942	0.972	0.973	0.967	0.990
O_7-H_{13}	0.947	0.947	0.939	0.969	0.969	0.962	0.987
$\angle C_1C_2C_6$	120.22	120.20	120.28	120.29	120.07	120.15	
$\angle C_1C_3C_5$	120.43	120.45	120.38	120.52	120.52	120.46	
$\angle C_2C_1C_3$	119.47	119.53	119.44	119.45	119.52	119.40	
$\angle C_2C_6C_{10}$	120.19	120.14	120.15	120.30	120.27	120.30	
$\angle C_3C_5C_{10}$	119.98	119.98	120.06	119.79	119.79	119.90	
$\angle C_3C_1O_4$	120.71	120.81	120.71	120.32	120.63	120.37	118.95
$\angle C_5C_3O_7$	124.01	124.02	124.14	124.65	124.52	124.73	122.35
$\angle C_1O_4H_9$	109.44	110.02	110.01	107.45	108.59	108.11	108.28
$\angle C_3O_7H_{13}$	111.09	111.73	111.74	109.57	110.55	110.39	109.57
$O_7 \cdots H_9$	2.164	2.175	2.172	2.121	2.152	2.131	
$O_4 \cdots O_7$	2.671	2.672	2.667	2.675	2.685	2.672	

[a] Reference 33.



2a 2b 2c

Figure 2. Possible conformers of 2-hydroxythiophenol (**2a**, syn−anti form; **2b**, syn−gauche form; **2c**, anti−anti form).

C_1-S_4 in conformer **2a** at all. On the other hand, the bond angle associated with the hydroxyl group which serves for the hydrogen donors in intramolecular hydrogen bonding shows somewhat interesting feature. The $C_3-O_7-H_{13}$ bond angle in conformer **2a** decreases noticeably when the electron correlation effect is taken into account at the B3LYP levels. These sorts of reduction of bond angles have been already seen in optimized geometries for 1,2-dihydroxybenzene as well as for other intramolecular hydrogen bonding systems such as 2-nitroresorcinol[8,10] and 4,6-dinitroresorcinol.[10] Therefore, one can deduce that these bond angles computed at the B3LYP levels are more reliable than those from RHF calculations even though there are no available experimental structural data. However, the $C_3-O_7-H_{13}$ bond angle in conformer **2b** is sensitive to electron correlation effects whereas the $C_1-S_4-H_9$ bond angle is not. These facts might suggest that the nature of intramolecular hydrogen bonding in conformer **2b** is somewhat different from that of intramolecular hydrogen bonding in conformer **2a**. Moreover, the computed $C_1-S_4-H_9$ bond angle of conformer **2b** at the B3LYP levels is ~2° larger than that of conformer **2a**. According to the hybridization model, the larger bond angle is caused by an increasing s character of hybrid orbitals. Therefore, the 3s orbital on the sulfur atom of conformer **2b** would contribute more to the bonding than that on the sulfur atom of conformer **2a**. In all possible hydrogen bonding conformers for both 1,2-dihydroxybenzene and 2-hydroxythiophenol, the computed endocyclic bond angles of the benzene rings are not much different from those of benzene. This means that intramolecular hydrogen bondings of our target molecules almost do not affect the resonance of the benzene ring.

The hydrogen bond distance $O \cdots H$ in conformer **2a** is computed to be about 2.5 Å at the RHF levels but decreases by about 0.25 Å at the B3LYP levels. It is because the torsional angle of the S−H group, which is computed to be about 40° at the RHF levels, is rotated down to about 0° at the B3LYP levels. The computed hydrogen bond distance at the B3LYP levels in conformer **2a** is somewhat longer than that of its oxygen analogue, that is, conformer **1a** (see Table 1). At the B3LYP levels, the hydrogen bond distance between sulfur and hydrogen atoms in conformer **2b** is computed to be ~2.4 Å, which is about 0.2 Å longer than that of conformer **2a**. It is still within the sum of van der Waals radii of hydrogen and sulfur atoms. Therefore, one can deduce that the predominance of conformer **2b** might be caused by the more effective interaction between sulfur and hydrogen atoms through the directional 3p orbital of the sulfur atom even though its $S \cdots H$ distance is somewhat longer than the $O \cdots H$ distance of conformer **2a**. As can be seen in Tables 1 and 2, the difference of the intramolecular hydrogen bonding distances between conformers **1a** and **2b** is about 0.3 Å at both RHF and B3LYP levels, which is just equal to the difference of van der Waals radii between oxygen and sulfur atoms.

The computed $S_4 \cdots O_7$ distance between sulfur and oxygen atoms in conformers **2a** and **2b** at both RHF and B3LYP levels are about 3 Å(see Tables 2 and 3). This value is somewhat longer than that of conformer **2c**, which is computed to be about 2.9 Å at both RHF and B3LYP levels, but still much shorter than the sum of van der Waals radii of sulfur and oxygen atoms. The same trend can be also found in comparing both two conformers of 1,2-dihydroxybenzene. In Table 1, the computed $O_4 \cdots O_7$ distance of conformer **1a** is about 2.68 Å at the B3LYP/6-31G** level, while this distance decreases to about 2.65 Å in conformer **1b**. Therefore, one can notice that the intramolecular hydrogen bonding in both molecules can somewhat contribute to relieve the nonbonding interaction between hydrogen bonding donor and acceptor groups.

^{1}H Chemical Shift of 2-Hydroxythiophenol. Table 4 shows both the computed ^{1}H NMR chemical shifts (ppm) at the RHF/6-31+G*//B3LYP/6-31+G* level and experimental data for 2-hydroxythiophenol. The previous experimental study [13] had shown that the predominance of conformer **2b** was confirmed by the interpretation of ^{1}H NMR spectra. Our results also show

TABLE 2: Geometrical Parameters for a Predominant Conformer, 2b, of 2-Hydroxylthiophenol at RHF and B3LYP Levels (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*
C_1-C_2	1.393	1.394	1.392	1.400	1.401	1.397
C_1-C_3	1.393	1.394	1.392	1.409	1.409	1.407
C_2-C_6	1.379	1.381	1.377	1.393	1.395	1.390
C_3-C_5	1.392	1.393	1.392	1.402	1.402	1.399
C_5-C_{10}	1.377	1.379	1.377	1.390	1.392	1.387
C_6-C_{10}	1.392	1.392	1.390	1.399	1.401	1.397
C_1-S_4	1.789	1.788	1.789	1.801	1.801	1.801
C_3-O_7	1.341	1.342	1.339	1.355	1.360	1.353
S_4-H_9	1.329	1.330	1.334	1.355	1.355	1.356
O_7-H_{13}	0.950	0.950	0.946	0.978	0.978	0.991
$\angle C_1C_2C_6$	121.05	121.04	121.03	120.56	120.60	120.58
$\angle C_1C_3C_5$	119.68	119.78	119.59	119.44	119.71	119.31
$\angle C_2C_1C_3$	119.36	119.29	119.44	119.79	119.60	119.85
$\angle C_2C_6C_{10}$	119.04	119.10	119.07	119.38	119.41	119.35
$\angle C_3C_5C_{10}$	120.08	120.06	120.14	120.08	119.99	120.18
$\angle C_2C_1S_4$	120.29	120.33	120.21	121.02	121.01	120.94
$\angle C_1C_3O_7$	123.29	123.17	123.33	122.75	122.59	122.77
$\angle C_1S_4H_9$	98.81	98.57	98.61	98.39	98.02	97.96
$\angle C_3O_7H_{13}$	110.31	110.76	110.86	107.44	108.18	108.16
$S_4\cdots H_{13}$	2.495	2.500	2.505	2.415	2.429	2.426
$S_4\cdots O_7$	3.061	3.061	3.060	3.050	3.053	3.047

TABLE 3: Some Important Geometrical Parameters for a Possible Conformer, 2a, of 2-Hydroxylthiophenol at RHF and B3LYP Levels (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*
C_1-C_2	1.386	1.388	1.385	1.399	1.401	1.396
C_1-C_3	1.394	1.394	1.393	1.406	1.407	1.404
C_3-C_5	1.384	1.388	1.384	1.396	1.397	1.394
C_1-S_4	1.780	1.779	1.780	1.785	1.783	1.784
C_3-O_7	1.351	1.352	1.348	1.372	1.375	1.370
S_4-H_9	1.324	1.324	1.329	1.346	1.347	1.348
O_7-H_{13}	0.948	0.947	0.939	0.970	0.969	0.964
$\angle C_1C_2C_6$	121.25	121.26	121.27	121.09	121.11	121.10
$\angle C_1C_3C_5$	120.12	120.19	120.01	120.13	120.35	120.06
$\angle C_2C_1C_3$	118.83	118.77	118.88	118.73	118.59	118.79
$\angle C_3C_1S_4$	122.11	121.94	122.35	122.27	122.24	122.46
$\angle C_5C_3O_7$	121.98	122.04	121.97	122.27	122.32	122.19
$\angle C_1S_4H_9$	98.15	97.89	98.10	96.40	96.42	96.13
$\angle C_3O_7H_{13}$	110.67	111.20	111.31	108.95	110.04	109.80
$O_7\cdots H_9$	2.525	2.444	2.569	2.253	2.253	2.241
$S_4\cdots O_7$	2.990	2.994	2.985	3.009	3.011	3.005

TABLE 4: ^1H Chemical Shifts (ppm) of 2-Hydroxythiophenol at the RHF/6-31+G*//B3LYP/6-31+G* Level

atoms	2a	2b	2c	exptl[a]
H_8	7.46	7.81	7.16	7.36
H_9	4.21	2.46	2.92	2.83
H_{11}	6.47	7.16	6.43	6.87
H_{12}	6.91	6.77	6.78	6.75
H_{13}	4.13	6.05	4.15	6.06
H_{14}	7.12	7.60	7.13	7.14

[a] Reference 13.

that calculated chemical shifts of conformer **2b** are in better agreement with experimental results than those of conformer **2a** as well as **2c**. The computed chemical shift of the S−H proton (H_9) in conformer **2c** is much closer to the experimental value than that of conformer **2b**. However, the computed value of the O−H proton (H_{13}) in conformer **2c** deviates considerably from the experimental value by about 2 ppm, while this value of conformer **2b** is in excellent agreement with the experimental chemical shift. The chemical shifts for the four other protons in the benzene ring of all three conformers are computed to be around 7 ppm, and they are not so different from each other. This means that they are not much affected by molecular conformations. The comparison of the chemical shift between S−H and O−H protons will provide us with some information about the torsion of the S−H group out of the benzene plane as well as about the extent of the electron donation through intramolecular hydrogen bonding in this molecule.

In comparison between conformers **2a** and **2c**, the chemical shift of the S−H proton (H_9) in conformer **2a** is computed to be 4.21 ppm, which is about 1 ppm larger than that of conformer **2c** with no hydrogen bond. On the other hand, the chemical shift of the O−H proton (H_{13}) in conformer **2b** is computed to be 6.05 ppm, which is about 2 ppm larger than that of conformer **2c**. Therefore, it can be assumed that the O−H proton of conformer **2b** is more deshielded than the S−H proton of conformer **2a** when the intramolecular hydrogen bonding is formed. Table 4 also shows that the S−H proton (H_9) of conformer **2b** is most shielded. Its computed chemical shift is 2.46 ppm, which is shifted to higher field by about 0.4 ppm than the value of conformer **2c** with no hydrogen bonding. In the previous experimental study,[35] a similar case has been also discussed by comparison of the chemical shift of the S−H proton between thiophenol and 2-hydroxythiophenol, and it is concluded that this chemical shift mainly arises not only from the magnetic anisotropy of the benzene ring but also from the electron donation from the O−H moiety. On the other hand, the computed chemical shift of the S−H proton in the conformer **2c** is not quite different from the experimental value for

TABLE 5: Total Atomic Charges for Possible Conformers of 1,2-Dihydroxybenzene and 2-Hydroxythiophenol at the RHF/6-31+G* Level

	1,2-dihydroxybenzene		1,2-dihydroxybenzene		
atoms	**1a**	**1b**	**2a**	**2b**	**2c**
C_1	0.317	0.314	−0.249	−0.327	−0.249
C_3	0.277	0.314	0.346	0.396	0.355
O_4	−0.769	−0.748			
S_4			0.031	−0.002	0.074
O_7	−0.788	−0.748	−0.774	−0.768	−0.760
H_9	0.531	0.506	0.165	0.140	0.117
H_{13}	0.520	0.506	0.517	0.523	0.514

thiophenol, which is 3.23 ppm,[34] whereas this value is computed to be 4.21 ppm in conformer **2a**. This relatively lower field shift can be attributed to the fact that this proton is somewhat deshielded owing to the intramolecular hydrogen bonding.

Population Analyses. To investigate the nature of intramolecular hydrogen bonds in these target moleculues more rigorously, we have performed natural population analyses [27] for 1,2-dihydroxybenzene as well as 2-hydroxythiophenol at the RHF/6-31+G* level. Total atomic charges for the possible conformers of 1,2-dihydroxybenzene and 2-hydroxythiophenol are summarized in Table 5. In 1,2-dihydroxybenzene, hydrogen atoms of two hydroxyl groups in conformer **1a** lose some charges while their adjacent oxygen atoms gain considerable charges. One can see that the intramolecular hydrogen bond makes the hydroxyl groups of conformer **1a** more polar than those of conformer **1b**. However, it is not as simple in 2-hydroxythiopheol as in 1,2-dihydroxybenzene.

In conformer **2a**, the atomic charge of the bridged hydrogen atom in the S−H group becomes more positive than that of the hydrogen atom in the S−H group in conformer **2c**, while the oxygen atom in the hydroxyl group becomes more negative. However, the charge of the hydrogen atom in the hydroxyl group in conformer **2a** remains almost unchanged as the intramolecular hydrogen bonding forms. This fact is somewhst different from bonding properties of its oxygen analogue, that is, conformer **1a** of 1,2-dihydroxybenzene. Therefore, one can notice that the S−H group loses some charges, while the hydroxyl group gains some charges through intramolecular hydrogen bonding. On the other hand, conformer **2b** shows that the bridged hydrogen atom in the O−H group loses charges, but the sulfur atom in the S−H group gains charges slightly. It is very interesting that the sign of charge on the sulfur atom in conformer **2b** reverses as the intramolecular hydrogen bond-(O−H···S) forms. Thus, this intramolecular hydrogen bond makes the S−H group a little polar. Therefore, two neighboring substituents in conformer **2b** become more polar than those in conformer **2a**. In particular, the S−H group in conformer **2b** is rather more polarized than that of conformer **2a**. This indicates that there is a strong relation between the polarization of two substituents and the stability of the hydrogen bonding conformer in this molecule.

Relative Energy Among Possible Conformers. The relative energies (kcal/mol) at various RHF and B3LYP levels for several possible conformers of 1,2-dihydroxybenzene and 2-hydroxythiophenol are summarized in Table 6. It can be shown that the results of both RHF and B3LYP calculations are not much different from each other. In 1,2-dihydroxybenzene, conformer **1a** is about 4.5 kcal/mol more stable than conformer **1b** at both RHF and B3LYP levels. In general, the hydrogen bonding energy is estimated theoretically by comparing the relative energies between the hydrogen bonding conformer and the reference conformer in which a hydroxyl group is rotated by 180° so as to prevent the hydrogen bonding. Therefore, one can estimate that the strength of hydrogen bond in 1,2-dihydroxybenzene is about 4 kcal/mol. The previous experiment has predicted that the hydrogen bond energy for this molecule is ∼2.29 kcal/mol. [16] There is some difference between the experimental value and theoretical one. Theoretical overestimation of the hydrogen bonding energy with respect to the experimental value might be ascribed to the O···O nonbonding interaction. In other words, the relatively shorter O···O distance of conformer **1b** relative to conformer **1a** makes much larger the difference of conformational energy between these two conformers.

TABLE 6: Relative Energies (kcal/mol) for 1,2-Dihydroxybenzene and 2-Hydroxythiophenol Conformers

calculational levels	**1a**	**1b**	**2a**	**2b**	**2c**
PM3	−1.80	0.0	−2.79	−3.44	0.0
RHF/6-31G**	−4.58	0.0	−1.01	−4.12	0.0
RHF/6-31+G*	−4.66	0.0	−1.15	−4.15	0.0
RHF/6-311G*	−4.83	0.0	−1.18	−4.51	0.0
RHF/6-311+G*	−4.88	0.0	−1.17	−4.02	0.0
B3LYP/6-31G**	−4.15	0.0	−0.90	−3.36	0.0
B3LYP/6-31+G*	−4.29	0.0	−1.18	−3.40	0.0
B3LYP/6-311G*	−4.52	0.0	−0.92	−3.64	0.0

In 2-hydroxythiophenol, the computed energies of conformer **2a** relative to conformer **2c** is approximately 1 kcal/mol at both RHF and B3LYP levels. This means that the energy gains by intramolecular hydrogen bonding in conformer **2a** are so small that it is doubtful whether the intramolecular hydrogen bonding exist. On the other hand, the theoretical works with the CNDO/2 method as well as an ab initio method with the minimal basis set could not explain experimental results [13] from which conformer **2b** is most favorable. For example, according to the semiempirical CNDO/2 results, conformer **2d** had the most stable conformation, and the computed energies for both conformers **2a** and **2b** were much higher than the energy of conformer **2d**. Calculational results at the STO-3G level are also unreliable to decide the relative stability of these conformers. PM3 calculations in this study show that the energy difference between conformers **2a** and **2b** is less than 1 kcal/mol. Such a small difference in energy cannot perfectly explain the predominance of conformer **2b.** However, in both RHF and B3LYP calculations, conformer **2b** has the most stable conformation and the hydrogen bonding energy for 2-hydroxythiophenol is calculated to be approximately 4 kcal/mol.

Conclusion

The molecular structures and the nature of intramolecular hydrogen bonding for both 1,2-dihydroxybenzene and 2-hydroxythiophenol are investigated by an ab initio method as well as the density functional theory. The optimized geometrical parameters associated with both hydroxyl and thiohydroxyl groups involved in intramolecular hydrogen bonding in these molecules are sensitive to change with respect to the electron correlation at the B3LYP levels. In 1,2-dihydroxybenzne, the computed geometrical parameters for the hydrogen bonding conformer **1a** at the B3LYP levels with a larger split valence basis set are much closer to experimental values than those at the RHF levels. Among three possible hydrogen bonding conformers for 2-hydroxythiophenol, computed ^{1}H NMR chemical shifts of conformer **2b** with the π type hydrogen bond between sulfur and hydrogen atoms through the directional 3p orbital on sulfur atom at the B3LYP/6-31+G* level are well matched with experimental NMR chemical shifts. The natural population analyses also support the reason the bonding characters of a predominant conformer in the intramolecular hydrogen bonding are so different from those of the others. On the other hand, the energy of intramolecular hydrogen bonding is estimated by making a comparison of molecular energies between two different conformations. In 1,2-dihydroxybenzene, the computed energy difference between conformers **1a** and **1b** is about 4 kcal/mol at both RHF and B3LYP levels. In 2-hydroxythiophenol, conformer **2b** with the π type hydrogen bonding is about 3 kcal/mol more stable than conformer **2a** with the common type hydrogen bonding at both RHF and B3LYP levels. Thus, it is confirmed that conformer **2b** is the most stable by both geometry optimizations and calculations of NMR chemical shifts.

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