Effects of Substituting Group on the Hydrogen Bonding in Phenol−H_2O Complexes: Ab Initio Study

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Calculations are presented for the ortho- and para-substituted phenol−H_2O complexes. A variety of conformers are predicted, and their relative energies are compared. Binding energies of the complexes are computed, and detailed analysis is presented on the effects of substitution on the strength of the hydrogen bonding in the complexes. F- and Cl- (NH_2- and OH-) substituted complexes are studied to analyze the effects of electron-withdrawing (electron-donating) groups. In para-substituted complexes, the electrostatic (inductive and resonance) effects influence the binding energies in opposite fashion, depending on whether the hydroxyl group is proton-donating or -accepting. The binding energy of the complex increases (decreases) by the electron-withdrawing substituent when the phenolic OH group is proton-donating (-accepting), and the reverse is true for the electron-donating substituents. For ortho-substituted complexes, direct involvement of the substituting group and the geometry change of the hydrogen bond should be invoked to elucidate the complicated pattern of the binding energy of the complexes. We also suggest that the frequency of the phenolic OH stretching mode of the complex may help elucidate the role of the OH group, determining whether the OH group is proton-donating or -accepting.

1. Introduction

Clusters or complexes of molecules have been given a lot of attention as intermediary structures lying between the isolated molecules and the fully solvated molecules in solution phase. Many solvent molecules may interact with the solute in solution phase, and the properties of the solute molecule in solution would depend on the configuration of the solvents around it in very complicated fashion. When only a small number of solvent molecules may affect the properties of solute in solution (for example, when a specific functional group of the solute interacts with solvent molecules), the solution phase may be approximated as clusters or complexes (called supramolecular approach),[1−17] since the interactions with the solvent molecules in the immediate vicinity of the functional group would largely determine the properties of the solution, while other solvent molecules may safely be considered as "spectators". Studying the influence of "microsolvation" on the structures and the reactivity of the "solute" molecule in the clusters or complexes may also help reveal fundamental information for the properties of molecules in the solvent environment.

The interactions between the hydroxyl group of the organic alcohol in aqueous solution is such a case, where the cluster model may be very useful to understand the effects of solvation. A computational study of the structures and binding energies of organic alcohol−water clusters can be a very useful guide to understanding the differential interactions (i.e., hydrogen bonding)[18,19] between a variety of functional groups with the water molecules, when combined with the experimental studies based on the infrared (IR) spectroscopy and the supersonic beam technique. The binding energies of these interesting clusters, when accurately computed, can yield direct estimation of the solvent−solute interactions measured, for example, by the chromatographic method,[20] on the molecular scale. Particularly interesting is the role of the differences in the structures of the functional groups in yielding differential hydrogen bonding with the water molecules. For example, in the analysis of the hydrogen bonding in phenol−$(H_2O)_n$ and benzyl alcohol−$(H_2O)_n$ ($n = 1-4$) clusters and in the corresponding clusters with the methanol molecules, we have found[21] that the differences in the binding energies of these clusters may largely be explained by the differences in the acidity and the hydrogen-bonding basicity of the organic alcohols and the "solvent" molecules in the system. This suggests that the electrostatic effects of the functional groups and the water or the methanol molecules are primarily important in determining the interactions. Other effects (such as steric) are considered to play minor role in this system; however, they may affect the strengths of the hydrogen bonding to a larger degree in other kinds of clusters. Since the binding energies of the weakly bound complexes can be measured directly as recently carried out by Leutwyler and co-workers[22] and by Chandler and co-workers,[23] calculations presented in this work would be quite useful for probing the strength of the hydrogen bonding.

In the present study, we investigate the effects of different types of interactions (inductive, resonance, steric, intramolecular hydrogen bonding, etc.) on the binding energies of the phenol derivative[24−26]−H_2O complexes[1−17] by studying the effects of substitution by several functional groups (−F, −Cl, −OH, and −NH_2) at ortho or para positions. In the para-substituted complexes, for which the effects may be safely considered as

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mostly electrostatic (including the resonance effects), the influence of the substituted functional groups depends on whether the hydroxyl group of the phenol moiety is proton-donating or -accepting: the binding energy of the complex increases (decreases) by the electron-withdrawing substituent when the phenolic OH group is proton-donating (-accepting), and the reverse is true for the elecron-donating substituents. For ortho substitution, however, the analysis of the binding energies in terms of any single factor would be in general very difficult, because other factors may also contribute. In addition to the electrostatic effects of the substituent, the intramolecular hydrogen bonding[27] and/or the steric hindrance may also affect the strengths of the hydrogen bonding in a very complicated fashion. In some cases, the presence of the substituents may even alter the local structures of the OH−water interactions, significantly affecting the magnitude of the interactions of the ortho-substituted complexes. In contrast to the para-substituted complexes, for which the binding energy is essentially determined by the strength of the hydrogen bonding between the phenolic OH and the water molecule, we find that the purely electrostatic effects of the substituting group at the ortho position may be dominant only when the geometries of the unsubstituted and the ortho-substituted phenol−water complexes are quite similar, giving a rough estimation of electrostatic effects. We also calculate the harmonic frequency of the phenolic OH stretching mode and find that the shifts of the harmonic frequencies in the complexes from those of bare phenol exhibit very different behavior, depending on whether the OH group is proton-donating or -accepting. The stretching frequency of the proton-donating OH in the complex significantly red shifts from that of bare phenol, while that of the proton-accepting OH group remains more or less unchanged. Thus, we suggest that measurement of the OH stretching frequency of the complex may help elucidate the role of the OH group in the complexes, determining whether the OH group is proton-donating or -accepting.

2. Computational Methods

In this study all the calculations were carried out using the GAUSSIAN 94 set of programs.[25] Bond lengths, angles, dipole moments, and harmonic frequencies are calculated along with the zero-point energies by employing the Moller−Plesset second-order perturbation (MP2)[29] method. For unknown reasons, using the diffuse functions for the hydrogen and/or other atoms does not give stationary structures for the planar phenyl ring structures (it yields an imaginary frequency for the ring-distorting mode). Therefore, we employ the 6-311G** basis set for the present work after systematically checking various other basis sets. The stationary conformers are obtained by verifying that all the harmonic frequencies are real. We employed the default convergence criteria for optimization in this work. The binding energies are computed as the difference between the energy of the complexes and the sum of the energies of the separated fragments with zero-point energies corrected. The basis set superposition error (BSSE) is estimated by employing the counterpoise method.[30]

3. Results

The effects of substituents on the hydrogen bonding in the aromatic alcohol−water complexes may be quite complicated to analyze. First, the substituting group may influence the hydrogen bonding between the hydroxyl and the water molecule through the phenyl ring by electrostatic factors such as inductive, field, or resonance effects.[31] In this case, the overall electron-withdrawing or electron-donating tendency of the substituent would be the critical factor to affect the strengths of the hydrogen bonds. For para-substituted phenols these effects will be most important, because the substituting group is rather isolated from the hydrogen bond. For ortho-substituted phenols, on the other hand, the substituting group is very close to the hydrogen bond between the hydroxyl and the water molecule, and thus may directly interact either with the hydroxyl group or the water molecule. In some instances, it is expected that the substituting group may alter the local structure of the complex near the hydrogen bond so that it may be completely different from that of the phenol−water complex.

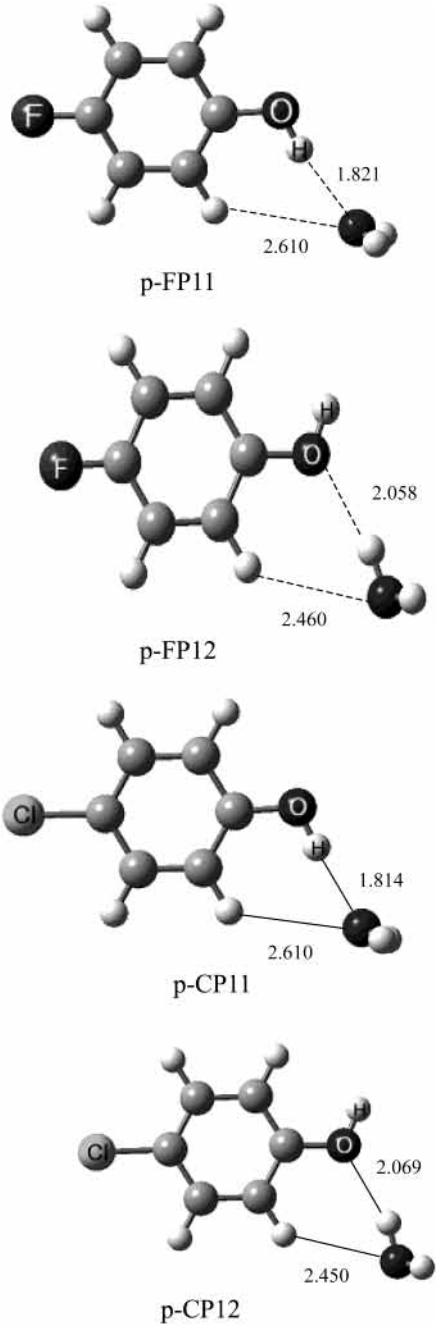

Figure 1. Computed structures of *p*-fluorophenol−H_2O (p-FP11 and p-FP12) and *p*-chlorophenol−H_2O complexes (p-CP11 and p-CP12).

Therefore we first investigate the binding energies of the para-substituted phenol−H_2O complexes to isolate the electrostatic effects of the substituting group through the phenyl ring. The computed structures and the energies of the *p*-fluorophenol−H_2O complexes are given in Figure 1 and Table 1. We obtain

TABLE 1: Calculated Energies, Zero-Point Energies (ZPE), and Binding Energies (BE)

	energy[a] (Hartree)	ZPE[a] (kcal/mol)	ΔE^a (kcal/mol)	BE[a] (kcal/mol)	role of phenolic OH group
H_2O	−76.26397	13.71			
phenol	−306.65428	64.95			
phenol−H_2O					
(P11)	−382.93428	80.64	0	8.07[b] (5.48)[c]	proton-donating
(P12)	−382.92986	80.49	+2.61	5.46(3.20)	proton-accepting
p-fluorophenol	−405.72475	60.03			
p-fluorophenol−H_2O					
(p-FP11)	−482.00546	75.77	0	8.47 (5.86)	proton-donating
(p-FP12)	−482.00026	75.55	+3.04	5.43 (2.52)	proton-accepting
p-aminophenol	−361.87858	75.62			
p-aminophenol−H_2O					
(p-AP11)	−438.15794	91.39	0	7.65 (5.09)	proton-donating
(p-AP12)	−438.15472	91.17	+1.85	5.80 (2.81)	proton-accepting
p-chlorophenol	−765.71075	59.00			
p-chlorophenol−H_2O					
(p-CP11)	−841.99188	74.75	0	8.72 (6.09)	proton-donating
(p-CP12)	−841.98607	74.47	+3.37	5.35 (2.45)	proton-accepting
hydroquinone	−381.72816	67.45			
hydroquinone- −H_2O					
(HQ11)	−458.00800	83.14	0	7.97 (5.38)	proton-donating
(HQ12)	−458.00418	83.08	+2.33	5.64 (2.67)	proton-accepting
o-fluorophenol					
(o-FP1)	−405.72547	60.19	0		
(o-FP2)	−405.72109	59.94	+2.50		
o-fluorophenol−H_2O					
(o-FP11)	−482.00511	75.86	0	7.87 (4.70)	proton-donating
(o-FP12)	−482.00225	75.71	+1.63	6.24 (3.58)	proton-donating
(o-FP13)	−482.00081	75.67	+2.50	5.37 (2.50)	proton-accepting
o-chlorophenol					
(o-CP1)	−765.71320	59.24	0		
(o-CP2)	−765.70886	59.00	+2.49		
o-chlorophenol−H_2O					
(o-CP11)	−841.99039	74.76	0	6.48 (3.84)	proton-donating
(o-CP12)	−841.98977	74.70	+0.33	6.15 (3.47)	proton-donating
(o-CP13)	−841.98849	74.68	+1.12	5.36 (2.49)	proton-accepting

[a] MP2/6-311G**. [b] Binding energy (not corrected for BSSE). [c] Binding energy (corrected for counterpoise BSSE, see text).

two isomers (p-FP11 and p-FP12), of which p-FP11 is of lower energy. In this isomer, the phenolic hydroxyl group is a proton-donor to the water molecule, while in p-FP12 it accepts a proton from the water. Since the fluorine is at the para position, direct involvement of the fluorine atom would be very difficult, and the difference in the binding energy relative to that of the phenol−H_2O complex may signify the electrostatic effects of the electron-*withdrawing* fluorine atom through the phenyl ring. It is also worth noting that the local structures of the complexes near the hydrogen bonds of the complexes p-FP11 and p-FP12 are quite similar to those of the corresponding phenol−H_2O complexes P11 and P12, respectively, shown in Figure 2 in which the distance between the two oxygen atoms is compared with the experimental value given by Gerhards, Kleinermanns, and co-workers.[32] Especially, the phenolic OH is proton-donating to the binding water molecule in p-FP11 and P11, while it acts as a proton-accepting group in p-FP12 and P12. The binding energies of the two para-substituted fluorophenol−H_2O complexes are computed to be 8.47 and 5.43 kcal/mol, respectively, while those of the phenol−H_2O complexes P11 and P12 are 8.07 and 5.46 kcal/mol, respectively, without correction for the BSSE. Comparing the binding energies of phenol−H_2O and of *p*-fluorophenol−H_2O complexes, it can be suggested that the para-substitution affects the binding energy of the complexes in opposite fashion depending on whether the phenolic OH is proton-donating or proton-accepting, since the binding energy of p-FP11 is larger than that of the phenol−H_2O complex P11, while the binding energy of p-FP12 is smaller than that of P12. The calculated binding energy of the phenol−H_2O complex P11 is rather larger than the experimental

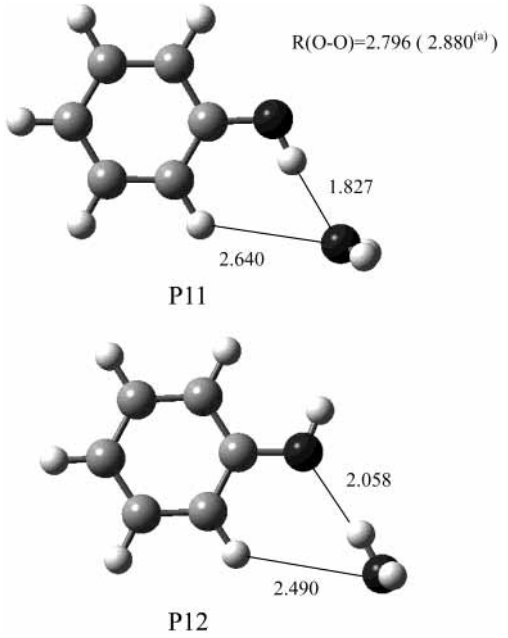

Figure 2. Computed structures of phenol−H_2O complexes (P11 and P12). (a) Experimental O−O length is taken from ref 32.

observation[33] (5.47 ± 0.09 kcal/mol), and the difference may be considered to be the BSSE. Thus, we estimate the BSSE by employing the counterpoise method. For the phenol−H_2O complex P11, the magnitude of the BSSE is calculated to be 3.89 kcal/mol. When it is fully considered, the BSSE-corrected

TABLE 2: Natural Population Analysis (NPA) for Para-Substituted Phenol−H_2O Complexes

	net charge of phenol moiety	net charge of water moiety	partial charge of O atom	partial charge of H atom
phenol			−0.72447	0.46436
phenol−$(H_2O)_1$				
P11	−0.01866	0.01866	−0.76122	0.50474
P12	0.00035	−0.00035	−0.75593	0.47480
p-fluorophenol			−0.72328	0.46524
p-fluorophenol−$(H_2O)_1$				
p-FP11	−0.01910	0.01910	−0.76046	0.50551
p-FP12	0.00011	−0.00011	−0.75499	0.47542
p-aminophenol			−0.72828	0.46150
p-aminophenol−$(H_2O)_1$				
p-AP11	−0.01787	0.01787	−0.76506	0.50181
p-AP12	0.00097	−0.00097	−0.76099	0.48036
p-chlorophenol			−0.72095	0.46669
p-chlorophenol−$(H_2O)_1$				
p-CP11	−0.01965	0.01965	−0.75765	0.50717
p-CP12	−0.00025	0.00025	−0.75226	0.47640
hydroquinone			−0.72674	0.46296
hydroquinone−(H_2O)				
HQ11	−0.01817	0.01817	−0.76383	0.50335
HQ12	0.00074	−0.00074	−0.75902	0.47376

binding energy of P11 becomes 4.18 kcal/mol, smaller than the experimental value. Since the estimation of the BSSE by the counterpoise method, however, is not undisputable, we adopt a heuristic approach in this work, by which we take 2/3 of the computed counterpoise-BSSE for the phenol−H_2O complex P11 for better agreement with experimental observation, and also for the other complex discussed below. When these corrections are carried out, the binding energies of P11 and P12 are 5.48 and 3.20 kcal/mol, respectively, and those of the *p*-fluorophenol−H_2O complexes p-FP11 and p-FP12 are 5.86 and 2.52 kcal/mol, respectively. Thus, these BSSE-corrected binding energies exhibit the same kind of behavior as that of the BSSE-uncorrected binding energies.

This interesting behavior of the binding energy can be understood by considering the fact that the electron-withdrawing effects of fluorine at the para position reduce the partial negative charge of the oxygen atom and increase the partial positive charge of the hydrogen atom of the phenolic OH group. As the result, the acidity of the hydrogen atom of OH increases. Thus, when the hydroxyl group acts as proton-donor (acid) as in the p-FP11 complex, the hydrogen bonding is strengthened by the fluorine atom at the para position. On the other hand, when the OH group is proton-accepting as in p-FP12, the binding energy decreases because the hydrogen bonding basicity of the oxygen atom of the hydroxyl group is reduced due to the substituted fluorine. It seems that the effects of the decrease in the partial negative charge at the oxygen atom of the OH group are larger than those due to the increase in the partial positive charge at the hydrogen atom, since the change (+0.38 kcal/mol) in the binding energies from P11 to p-FP11 is smaller than that (−0.68 kcal/mol) from P12 to p-FP12. To confirm these latter discussions, we carry out the Natural Population Analysis (NPA) for the para-substituted phenol−H_2O complexes. The calculated charge transfer and the partial charges of the oxygen and the hydrogen atoms of the phenolic OH group are presented in Table 2. It seems that the results of the NPA are in good agreement with our explanations given above for the changes in the binding energies of the complexes due to substitution at the phenyl ring. For example, the partial positive charge of the hydrogen atom of the hydroxyl group at the phenyl ring increases from +0.50474 (P11) to +0.50551 (p-FP11) upon substitution by a fluorine atom at the para position, thus increasing the acidity of the hydrogen atom. The net charge transfer from the water to the phenol moiety also increases from −0.01866 to −0.01910, indicating that more negative charge is transferred from the water to the phenol moiety. As the result, the hydrogen bonding is strengthened in the phenol−H_2O complex containing a proton-donating OH group upon substitution by a fluorine atom at the para position. On the other hand, the partial negative charge of the oxygen atom of the hydroxyl group at the phenyl ring decreases from −0.75593 in the proton-accepting phenol−H_2O complex (P12) to −0.75499 (p-FP12) upon substitution by a fluorine atom at the para position. The net charge transfer from the water to the phenol moiety decreases from +0.00035 to +0.00011. Thus, the hydrogen-bonding basicity of the oxygen atom of the OH group is reduced due to the substituted fluorine, thus decreasing the binding energy of the proton-accepting phenol−H_2O complex, as discussed above.

Figure 1 also depicts the *p*-chlorophenol−H_2O complexes (p-CP11 and p-CP12), in which the hydroxyl group acts as proton donor and acceptor, respectively. Table 1 shows that the BSSE-corrected binding energies (6.09 and 2.45 kcal/mol for p-CP11 and p-CP12, respectively) for these chlorophenol−H_2O complexes change to a larger degree from those of the corresponding phenol−H_2O complexes than for the *p*-fluorophenol−H_2O complexes. This is due to the fact that, although the inductive and field effects of fluorine are larger than those of chlorine, the resonance effects reduce the electron-withdrawing strength of the inductive and field effects of the substituting −F group more than in the case of the substituting −Cl group, making the chlorine atom overall more electron-withdrawing.[31] Thus, our computed binding energies of *p*-chlorophenol−H_2O complexes are in line with the fact that the overall electron-withdrawing tendency of the −Cl group is larger than that of the −F group. The larger electron-withdrawing effects of the −Cl group relative to the −F group may also be seen in the NPA analysis given in Table. 2. For example, the partial positive charge of the hydrogen atom of the hydroxyl group at the phenyl ring of the proton-donating complexes increases from +0.50551 (p-FP11) to +0.50717 (p-CP11), thus increasing the acidity of the hydrogen atom and the magnitude of hydrogen bonding.

By the same reasoning, substitution by an electron-*donating* group at the para position is expected to give effects that are opposite to the case of *p*-flurophenol−H_2O or *p*-chlorophenol−

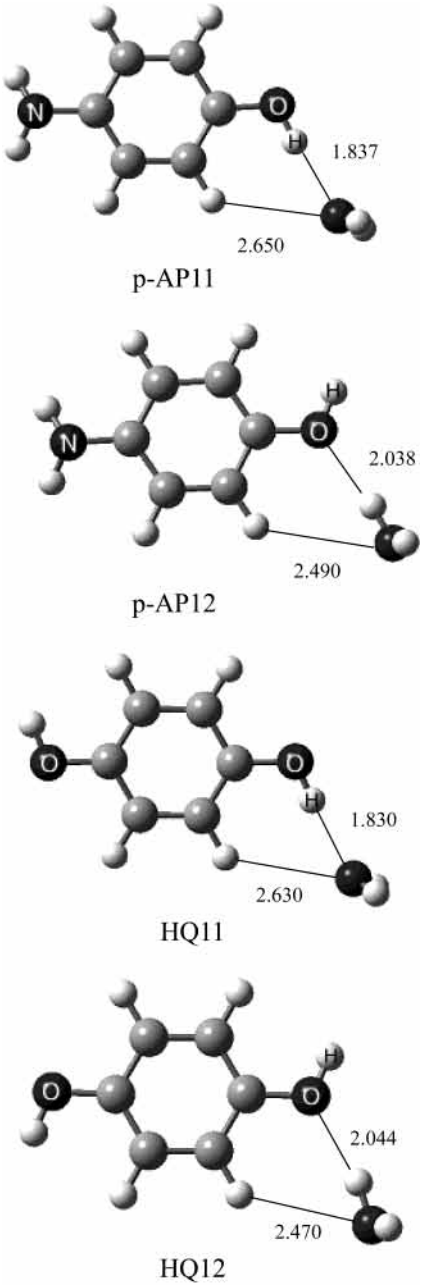

Figure 3. Computed structures of *p*-aminophenol−H_2O (p-AP11 and p-AP12) and hydroquinone−H_2O complexes (HQ11 and HQ12).

H_2O complexes, decreasing (increasing) the bonding energies of the complexes containing the proton-donating (-accepting) hydroxyl group. To confirm this prediction, we carry out calculations for the *p*-aminophenol−H_2O complexes (p-AP11 and p-AP12) as shown in Figure 3. We find two isomers of the *p*-aminophenol−H_2O complex. The BSSE-uncorrected binding energy (7.65 kcal/mol) of p-AP11 is smaller than that (8.07 kcal/mol) of the phenol−H_2O complex P11, while the binding energy (5.80 kcal/mol) of p-AP12 is larger than that (5.46 kcal/mol) of P12. The changes in the binding energies of the phenol−H_2O complexes upon substitution by an electron-donating group may also be understood by invoking the changes in the acidity of the hydrogen atom and the hydrogen-bonding basicity of the oxygen atom of the phenolic OH group. The results of NPA presented in Table 2 also seem to corroborate these points: the acidity (hydrogen-bonding basicity) of the hydrogen (oxygen) atom decreases (increases) upon substitution by a electron-donating group at the para position for the proton-donating phenol−H_2O complexes, while the reverse is true for the proton-accepting complexes. A similar trend is also seen for the hydroquinone−H_2O complex (HQ11 and HQ12) whose structures and (uncorrected) binding energies (7.97 and 5.64 kcal/mol for HQ11 and HQ12, respectively) are also given in Figure 3 and Table 1, respectively, although the binding energies for these latter change to a lesser degree from those of the corresponding phenol−H_2O complexes than for the *p*-aminophenol−H_2O complexes. For the BSSE-corrected binding energies of the *p*-aminophenol−H_2O and *p*-hydroxyphenol (hydroquinone)−H_2O complexes containing a proton-accepting hydroxyl group, however, the effects of the BSSE are more subtle, and we observe behavior that is in disagreement with that of the uncorrected binding energies: the BSSE-corrected binding energies of p-AP12 and HQ12 (2.81 and 2.67 kcal/mol, respectively) are smaller than that (3.20 kcal/mol) of the phenol−H_2O complex P12. It seems that the counterpoise method may overestimate the real BSSE in this case, and that a smaller portion of the counterpoise BSSE must be employed than that (2/3) invoked for the *p*-fluoro- and *p*-chlorophenol−water complexes (p-FP12 and p-FP12) containing the electron-withdrawing substituents discussed above, so that more accurate binding energies may be obtained for these complexes with electron-donating substituting groups.

We find two isomers for *o*-fluorophenol as shown in Figure 4. Of the two structures, the isomer displaying intramolecular hydrogen bonding (o-FP1) is of the lower energy. The difference in the energy (2.50 kcal/mol) of the two isomers may be considered as the approximate magnitude of the intramolecular hydrogen bond between OH and F, since other parts of the molecules are more or less similar. The structures of the *o*-fluorophenol−H_2O complexes are shown in Figure 4. In the first isomer (o-FP11), which is of the lowest energy, the hydroxyl group and the fluorine atom form an intramolecular hydrogen bond, and the water molecule bonds both to the hydroxyl and the fluorine atom. In this isomer, the hydroxyl group acts as proton donor both to the water and the fluorine atom. The length of the hydrogen bond between the water molecule and the hydroxyl group is 1.780 Å, while the H−F distance is 2.420 Å. In the second conformer (o-FP12), the hydroxyl group is also proton-donating, but does not form an intramolecular hydrogen bond with the fluorine atom. The length (1.808 Å) of the water−hydroxyl hydrogen bond and the H−F distance (2.640 Å) are a bit larger than those in the isomer o-FP11, indicating weaker interactions, and the water molecule is approximately perpendicular to the phenyl ring in this conformer. The structure of the corresponding phenol−H_2O complex (P11), in which the phenolic OH is a proton donor, is given in Figure 2. Since the hydroxyl group and the fluorine atom form an intramolecular hydrogen bond, this latter complex (P11) is more similar to o-FP11 than to the complex o-FP12, although the orientations of the water molecule relative to the phenyl ring are quite different.

The BSSE-corrected binding energies of these two isomers are 4.70 and 3.58 kcal/mol, both of which being smaller than that (5.48 kcal/mol) of the phenol−water complex (P11) with the proton-donating OH group. Considering that the substitution by a fluorine atom at the para position *increases* the binding energy of the complex relative to that of the phenol−water complex P11 with the proton-donating OH group, this latter observation strongly suggests that noninductive effects may also play a significant role affecting the binding energies of ortho-substituted complexes relative to unsubstituted phenol−water complexes. The effects of the substituents in this case seem to

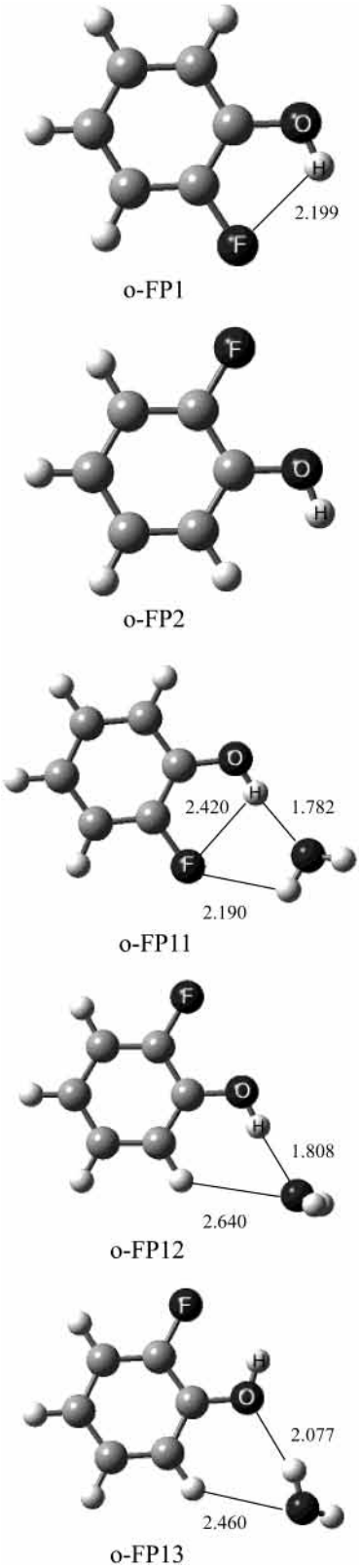

Figure 4. Computed structures of *o*-fluorophenol (o-FP1 and o-FP2) and *o*-fluorophenol−H_2O complexes (o-FP11, o-FP12, o-FP13).

be quite complicated, due to the fact that they are very close to the hydrogen bonds, directly interacting with the hydroxyl group or the water molecule, even altering the structure of the complex near the hydrogen bond. Comparing the structures of P11 and o-FP11, it can be seen that both of them contain an intramolecular hydrogen bond between the phenolic OH and hydrogen, and fluorine atom, respectively. The orientation of the water molecule relative to the phenyl ring is, however, different in the two complexes. In P11, the α-hydrogen (adjacent to the OH group, forming an intramolecular hydrogen bond with it) interacts only with the oxygen atom of the water molecule, while the fluorine atom in o-PF11 interacts with both the hydrogen and oxygen atoms of the water molecule. Consequently, the water molecule in the o-FP11 complex rotates away from the position perpendicular to the phenyl ring of P11, lying in an oblique position relative to the phenyl ring, making the hydrogen bond O_p-H-O_w a bit more bent than in P11 (O_p and O_w denote the oxygen atom of the phenolic OH group and the water molecule, respectively). The angle is 177.1° and 171.0° in P11 and o-FP11, respectively. It is also worth noting that the fluorine atom in o-FP11 may directly interact with the hydrogen atom of the hydroxyl group, partially relaxing the polarization of the hydroxyl, also rendering the hydrogen bond weaker. These two effects (that is, bending of the O_p-H-O_w bond and partial relaxation of the charge separation of the hydroxyl group) seem to yield a slightly smaller binding energy of o-FP11 relative to that of P1, despite the assumed gain in the binding energy due to the inductive effect of the fluorine atom at the ortho position. On the other hand, in the complex o-FP12, the water molecule is bonded only to the hydroxyl group. Thus, the absence of the bonding between the water molecule and the fluorine atom, and that between −F and the α-hydrogen, seems to make the binding energy significantly smaller than that of o-FP11 that displays the interactions between the water and the fluorine (α-hydrogen) atom. We may obtain some information for the inductive effects of the substituted fluorine at the ortho position by comparing the binding energies of p-FP1 (see Figure 1) and o-FP12. While the binding energy of p-FP11 gives a rough estimate of the electrostatic effects at the para position, that of o-FP12 is affected both by the electrostatic effects and by the intramolecular hydrogen bond between OH and F. Considering that the approximate magnitude of the intramolecular interaction in o-FP1 (that is, the energy difference between o-FP1 and o-FP2) is 2.50 kcal/mol, we may estimate that the electrostatic effects amount to −0.67 kcal/mol (−0.60 kcal/mol, when the BSSE is considered). Thus, the magnitude of the electrostatic effects of ortho-substitution by a fluorine atom seems to be larger than that (−0.38 kcal/mol) due to substitution at the para position.

The phenol−H_2O complex corresponding to the *o*-fluorophenol−H_2O complex o-FP13 shown in Figure 4 is P12 as depicted in Figure 2, in the sense that the hydroxyl group *accepts* a proton from the water molecule. The BSSE-corrected binding energy of o-FP13 is computed to be 2.50 kcal/mol, being smaller than that of the corresponding phenol−H_2O complex (P12). This behavior of the binding energy is similar to that of *p*-flurophenol−H_2O complex (p-FP12) containing a proton-accepting hydroxyl group. For o-FP13, the overall effects of the substitution by a fluorine atom at the ortho position are almost identical to those of p-FP12, yielding a slightly smaller binding energy than the corresponding phenol−H_2O complex P12. This does not mean, however, that the inductive effects are dominant for determining the binding energy of o-FP13 relative to that of P12 as in the case of p-FP12. There exists a geometrical difference between o-FP13 and P12. For example, the hydroxyl group does not interact with the α-hydrogen atom in P12, while it forms an intramolecular hydrogen bond with the fluorine atom in o-FP13. It may be that the inductive effects are smaller in o-FP13 than in p-FP12, and the remainder of the decrease in the binding energy of o-FP13 relative to that of P12 is caused

by the effects of the intramolecular interactions between the hydroxyl group and the fluorine atom.

We find two isomers for *o*-chlorophenol as shown in Figure. 5. The structures of the two isomers are similar to those of the *o*-fluorophenol molecule. The structure of lower energy isomer, o-CP1, forms intramolecular hydrogen bonding between the hydroxyl group and the chlorine atom. All of the atoms of the two isomers lie in a plane. The difference of energy between the two isomers, 2.49 kcal/mol, is similar to that (2.50 kcal/mol) between the two *o*-fluorophenol isomers. The difference in energy of the two *o*-chlorophenol isomers o-CP1 and o-CP2 may also be considered as approximate magnitude of the intramolecular hydrogen bonding as in the case of *o*-fluorophenol. The structures of the *o*-chlorophenol−H_2O complexes are shown in Figure 5. In the isomer o-CP11, which is of the lowest energy, the hydroxyl group and the chlorine atom do not form an intramolecular hydrogen bond, while in the isomer o-CP12 they do. The lengths of the hydrogen bonds between the hydroxyl group and the water are 1.803 and 1.800 Å, respectively, for o-CP11 and o-CP12, a bit larger than that of the lowest energy isomer (o-FP11) of the *o*-fluorophenol complex. It is interesting to note that the distance (2.878 Å) between the hydrogen atom of water and the chlorine atom in o-CP12 is larger than that (2.193 Å) of o-FP11. This difference seems to be due to the difference in the size of Cl and F. In the lowest-energy isomer o-CP11, the hydroxyl group is also proton-donating, but does not form an intramolecular hydrogen bond with the chlorine atom. The length (1.803 Å) of the hydrogen bond is similar to that (1.808 Å) of o-FP12.

The binding energies of these two isomers (o-CP11 and o-CP12) of *o*-chlorophenol−H_2O complexes are 3.84 and 3.47 kcal/mol, respectively. Both of them are significantly smaller than that (5.48 kcal/mol) of the phenol−water complex (P11) with the proton-donating OH group, in contrast to the *p*-chlorophenol−H_2O complexes whose binding energies are larger than that of P11. The noninductive effects may also affect the binding energies of these *o*-chlorophenol−H_2O complexes. Since the difference in the energies of the two *o*-chlorophenol isomers (o-CP11 and o-CP12) is 2.49 kcal/mol, the magnitude of the inductive effects in o-CP11 may be estimated to be −0.90 kcal/mol (−0.85 kcal/mol, when the BSSE is considered) similarly to the case of the *o*-fluorophenol−H_2O complexes. Thus, the estimated magnitude of the electrostatic effects of a chlorine atom at the ortho position on the binding energy seem to be lager than that of fluorine substitution at the ortho position −0.67 (−0.60) kcal/mol. This fact is also explained by the resonance and field effects:[31] The electronegativity of fluorine, a rough parameter of the inductive effect, is larger than that of chlorine, while the resonance effect of fluorine is smaller than that of chlorine. In this case, the resonance effect seems to be more important than the field effect. The *o*-chlorophenol−H_2O complex with the hydroxyl group acting as proton-acceptor (o-CP13), is also depicted in Figure 5. The binding energy is computed to be 2.49 kcal/mol. For o-CP13, the overall effects of substitution by a chlorine atom at the ortho position are almost identical to those of p-CP11 except the intramolecular effect.

The dipole moments of the clusters are of considerable interest recently, because the dipole binding of electron to the clusters may give the structures of the parent clusters. Table 3 presents the dipole moments of the complexes studied in this work. It is expected that the structures of most of the substituted phenol−water complexes listed in Table 3 with a dipole moment larger than 2.6 D may be experimentally determined by the dipole binding technique.[34] Table 3 also gives the calculated rotational

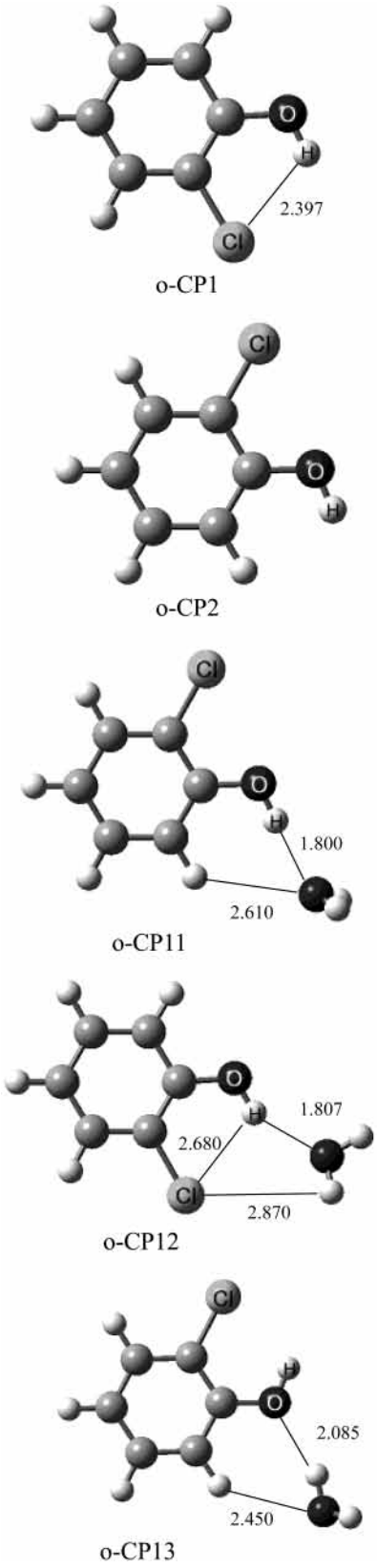

Figure 5. Computed structures of *o*-chlorophenol (o-CP1, o-CP2) and *o*-chlorophenol−H_2O complexes (o-CP11, o-CP12, o-CP13).

constants and the (unscaled) harmonic frequencies of the hydroxyl stretching mode of the bare phenol, substituted phenols, and the corresponding complexes, and those of the symmetric and the asymmetric stretching modes of the binding water molecule in the complexes. These harmonic frequencies may also give very instructive information on the strengths of

TABLE 3: Calculated Dipole Moments (μ) and Harmonic Frequencies of Phenolic OH Stretching (ν_{OH}), Symmetric (ν_{Sym}), and Asymmetric (ν_{Asym}) Stretching Modes of Water

	μ (Debye)	rotational constants (GHz)	ν_{OH} (cm^{-1})	ν_{sym} (cm^{-1})	ν_{asym} (cm^{-1})
H_2O	2.10	(785.2, 449.9, 286.0)		3908.1[6.21]	4015.9[33.54]
phenol	1.34	(5.637, 2.609, 1.784)	3883.5[63.42]		
phenol−H_2O					
(P11)	4.31	(4.230, 1.139, 0.901)	3706.7[685.75]	3887.1[17.63]	3997.1[74.87]
		(4.291, 1.092, 0.874)[a]			
(P12)	3.38	(3.932, 1.176, 0.909)	3884.7[65.24]	3870.0[85.52]	3973.8[80.30]
p-fluorophenol	1.99	(5.623, 1.446, 1.150)	3885.7[66.36]		
p-fluorophenol−H_2O					
(p-FP11)	5.50	(3.659, 0.784, 0.647)	3706.1[695.75]	3888.2[18.35]	3997.6[76.70]
(p-FP12)	3.39	(3.230, 0.815, 0.656)	3887.9[69.34]	3868.6[81.82]	3973.6[82.47]
p-aminophenol	2.02	(5.566, 1.470, 1.165)	3888.9[62.22]		
p-aminophenol−H_2O					
(p-AP11)	3.75	(3.645, 0.794, 0.655)	3722.5[669.94]	3887.0[16.27]	3997.1[72.71]
(p-AP12)	3.61	(3.311, 0.828, 0.665)	3890.9[68.11]	3865.0[97.73]	3971.3[80.61]
p-chlorophenol	2.27	(5.629, 0.970, 0.827)	3883.8[74.75]		
p-chlorophenol−H_2O					
(p-CP11)	5.92	(3.430, 0.580, 0.498)	3694.6[766.01]	3886.7[19.98]	3996.2[78.06]
(p-CP12)	3.52	(3.049, 0.603, 0.504)	3884.5[75.16]	3870.9[76.20]	3974.6[83.73]
hydroquinone	0.00	(5.605, 1.476, 1.168)	3888.6[128.04]		
			3889.8[0.00]		
hydroquinone−H_2O					
(HQ11)	3.55	(3.656, 0.796, 0.656)	3717.4[681.66]	3888.6[17.73]	3998.5[74.36]
(HQ12)	2.09	(3.332, 0.828, 0.665)	3890.7[45.84]	3864.8[92.33]	3971.3[80.51]
o-fluorophenol					
(o-FP1)	0.79	(3.330, 2.220, 1.332)	3862.1[102.13]		
(o-FP2)	2.62	(3.295, 2.230, 1.330)	3888.6[75.73]		
o-fluorophenol−H_2O					
(o-FP11)	2.83	(3.018, 1.086, 0.827)	3603.1[923.95]	3888.2[20.39]	3996.0[84.39]
(o-FP12)	4.93	(2.306, 1.092, 0.744)	3686.3[762.56]	3886.9[19.20]	3996.0[77.78]
(o-FP13)	2.54	(2.244, 1.114, 0.747)	3859.5[122.50]	3873.9[51.37]	3975.4[79.13]
o-chlorophenol					
(o-CP1)	0.82	(2.964, 1.543, 1.014)	3831.8[92.37]		
(o-CP2)	2.83	(2.958, 1.545, 1.015)	3880.8[75.51]		
o-chlorophenol−H_2O					
(o-CP11)	5.18	(1.586, 1.001, 0.616)	3674.6[797.93]	3886.1[20.43]	3995.0[78.70]
(o-CP12)	3.21	(2.054, 0.977, 0.714)	3633.7[740.96]	3887.0[15.08]	3997.7[65.31]
(o-CP13)	2.42	(1.632, 0.975, 0.612)	3822.9[107.44]	3874.1[58.60]	3975.4[82.53]

[a] Experimental rotational constants of the phenol−H_2O complex are from ref 32.

TABLE 4: Harmonic Frequencies of Phenolic OH Stretching (ν_{OH}), and Symmetric (ν_{Sym}) and Asymmetric (ν_{Asym}) Stretching Modes of Water

	HF/6-31G	HF/6-31+G**	BLYP/6-31G**	MP2/6-311G**	MP2/ cc-pVDZ	expt[a]
			Water			
ν_{sym}	3988.3	4145.9	3663.8	3908.1	3853.3	3657
ν_{asym}	4145.3	4262.5	3784.2	4015.9	3972.6	3756
			Phenol			
ν_{OH}	4050.1	4196.3	3667.9	3883.5	3831.2	3657
			Phenol−H_2O (P11)			
ν_{OH}	3849.2	4075.4	3465.4	3706.7	3646.3	3524
ν_{sym}	4001.9	4143.4	3664.0	3887.1	3834.7	3650
ν_{asym}	4151.8	4258.6	3777.7	3997.1	3951.8	3748
			Phenol−H_2O (P12))			
ν_{OH}	4046.5	4192.6	3677.6	3884.7	3833.0	
ν_{sym}	3930.6	4128.0	3588.9	3870.0	3820.5	
ν_{asym}	4110.8	4242.9	3751.4	3973.8	3931.5	

[a] Experimental frequencies of phenol−water complexes are from refs 35 and 36, and those of water are from ref 37.

the interactions in the complexes, along with the bond lengths and the binding energies as discussed above. The harmonic frequencies of the hydroxyl group in the substituted phenol−water complexes may considerably change from those of the corresponding bare substituted phenol, which may indicate that the OH bond weakens when forming a hydrogen bond with the water molecule. We find that the harmonic frequency of the stretching mode of the proton-*donating* OH group in the substituted phenol moiety in the complexes significantly decrease from that of bare substituted phenol. For example, while the OH stretching mode frequency of the *p*-fluorophenol is computed to be 3886 cm^{-1}, that of the corresponding complex p-FP11 is calculated to be only 3706 cm^{-1}. A similar trend is also seen for the other complexes containing the proton-donating OH group, the decrease being in the range of 160−260 cm^{-1}. The experimental decrease in the harmonic frequencies would be smaller, when the appropriate scaling factor is employed. On the other hand, the harmonic frequency of the stretching mode of the proton-*accepting* OH group in the substituted phenol moiety in the complexes exhibits very different behavior,

remaining more or less the same as that of bare substituted phenol: The harmonic frequency of the *p*-fluorophenol−water complex p-FP12, which possesses a proton-accepting phenolic OH group, is computed to be 3888 cm^{-1}, while that of bare *p*-fluorophenol is computed to be 3886 cm^{-1}. A similar pattern is also observed for all the other complexes with a proton-accepting phenolic OH group. To confirm this pattern, we also employ other methods (HF/6-31G, HF/6-31+G** and BLYP/6-31G**) as given in Table 4 to compute the OH stretching frequencies of substituted phenol−water complexes. The experimental frequencies of the phenol−H_2O complex observed by Mikami and co-workers,[35,36] and those of water[37] are also presented in Table 4. It can be seen that the stretching frequency of proton-donating OH in the complex P11 significantly decreases from that of bare phenol at all levels of theory reported in Table 4, while that of P12 containing the proton-accepting OH group slightly decreases or increases from the case of bare phenol depending on the method. The slight blue shift of the OH stretching frequencies in Table 3, computed by the MP2/6-311G** method, is therefore not very clear, although the change in either direction would be very small. This interesting difference in the behavior of frequency shifts in the complexes containing a proton-donating and proton-accepting OH group may be very instructive for experimentally elucidating the structures of the substituted phenol−water complexes by the infrared spectroscopic methods. The harmonic frequencies of the hydroxyl group may also give a rough estimate of the effects of intramolecular bonding on the infrared frequency. For example, the difference (27 cm^{-1}) between the OH stretching frequencies of o-FP1 and o-FP2 (3862 and 3889 cm^{-1}, respectively) may result mostly from the effects of the intramolecular hydrogen bonding between the hydroxyl group and the F atom. All the symmetric and asymmetric stretching frequencies of the water moiety in the complexes decrease from the corresponding mode of the free water, as presented in Table 3.

4. Conclusions

The effects of substitution at the para position are almost entirely inductive, and the analysis of the binding energies of the para-substituted phenol−H_2O complexes is quite straightforward: When a electron-withdrawing group is substituted at the para position, the binding energy of the complex containing proton-donating (-accepting) hydroxyl group increases (decreases), while the reverse is true for electron-donating substituents. For the ortho-substituted complexes, various effects are present to affect the strength of the hydrogen bonds in the complexes. In addition to the inductive effects, the substituents may directly bond with the hydroxyl group or the water molecule, or induce considerable change in the local structure near the hydrogen bonds. Experimental studies on these complexes would be highly intriguing and desirable. We have also demonstrated that the infrared frequencies of the complexes may help elucidate the structures of the substituted phenol−water complexes by the infrared spectroscopic methods, especially for determining whether the phenolic OH group is proton-donating or -accepting.

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