Phenol vs Water Molecule Interacting with Various Molecules: σ-type, π-type, and χ-type Hydrogen Bonds, Interaction Energies, and Their Energy Components

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The nature of interactions of phenol with various molecules (Y = HF, HCl, H_2O, H_2S, NH_3, PH_3, MeOH, MeSH) is investigated using ab initio calculations. The optimized geometrical parameters and spectra for the global energy minima of the complexes match the available experimental data. The contribution of attractive (electrostatic, inductive, dispersive) and repulsive (exchange) components to the binding energy is analyzed. HF favors σ_O-type H-bonding, while H_2O, NH_3, and MeOH favor σ_H-type H-bonding, where σ_O-/σ_H-type is the case when a H-bond forms between the phenolic O/H atom and its interacting molecule. On the other hand, HCl, H_2S, and PH_3 favor π-type H-bonding, which are slightly favored over σ_O-, σ_H-, σ_H-type bonding, respectively. MeSH favors χ_H-type bonding, which has characteristics of both π and σ_H. The origin of these conformational preferences depending on the type of molecules is elucidated. Finally, phenol−Y complexes are compared with water−Y complexes. In the water−Y complexes where σ_O/σ_H-type involves the H-bond by the water O/H atom, HF and HCl favor σ_O-type, H_2O involves both σ_O-/σ_H-type, and H_2S, NH_3, PH_3, MeOH, and MeSH favor σ_H-type bonding. Except for HF, seven other species have larger binding energies with a phenol molecule than a water molecule.

Introduction

Intermolecular interactions are very important in understanding organic, organometallic, and biomolecular structures, supramolecular assembly, crystal packing, reaction selectivity/specificity, and drug−receptor interactions.[1] On the basis of these interaction forces, not only theoretical design but also experimental realization of novel functional molecules, nanomaterials, and molecular devices has become possible.[2] Thus, the study of the fundamental intermolecular interactions and new types of interaction is very important for aiding self-assembly synthesis and nanomaterials design as well as for understanding molecular cluster formation.[3] In particular, novel types of interactions involving aromatic rings have been an important subject in the past decade.[4] In this regard, it is interesting to compare the binary complexes of phenol with the water analogues.

Phenol is a common chemical and a prototypical aromatic chromophore. The phenolic group is ubiquitous in nature. Its antioxidant property as a biomimic of α-tocopherol, a major constituent of vitamin E, has attracted tremendous academic and industrial interests for designing antioxidant materials with phenolic constituents.[5] In polymer industry phenol and formaldehyde are polymerized to produce Bakelite. Phenol is amphoteric and acts as both Lewis acid and base involving in H-bonding as a proton donor (Lewis acid) as well as a proton acceptor (Lewis base). Phenol exists in keto and enol tautomeric forms, but it is known that in solvent medium the enol form is the exclusive structure.

The interaction of phenol with an interacting molecule (Y) (phenol−Y) is intriguing. The hydrogen-bonded complexes of phenol are examples of interaction with aromatic acid, serving as a prototype for tyrosine residues in proteins interacting with water. The phenol−Y systems are useful models for microsolvated phenol clusters. The phenol−solvent potential-energy surfaces are valuable for building model potentials in biomolecular simulations in solvent environment. Among the phenol−Y systems the most widely studied systems are phenol−H_2O and phenol−NH_3. There are interesting studies on the σ and π complexes of phenol−H_2O.[6−11] Phenol−NH_3 clusters were also widely studied by various spectroscopic techniques and theoretical methods.[6,12−15] Very recently, the molecular mechanism of photoacidity of phenol−NH_3 has been elucidated.[16] The interpretation of vast spectroscopic data on phenol−water and phenol−ammonia and their cations has been greatly facilitated by ab initio calculations.

However, phenol−MeOH is rarely studied.[17] The latter system can be a model of the cysteine side chain of glutathione, which is useful for examining the role of active site tyrosine in glutathione S-transferases.[18] Special mention should be made about MeOH and MeSH. In addition to forming conventional H-bonds, the Me group can interact with phenol via dispersive forces in π−H-bonded complexes. Thus, the structures will reflect a balance between σ and π interaction. However, despite detailed studies of π−H complexes for benzene and some of its derivatives,[19] little attention has been paid to the capability of phenol for the π−H interactions. In the case of π−H interactions[20] it requires high-level calculations with large basis sets to obtain reliable structures and binding energies. In addition, to clearly understand the nature of the interactions, quantitative analysis of interaction components should be made.

It needs to be mentioned here that some of the substances discussed here, e.g., HF, which is extremely hazardous, are

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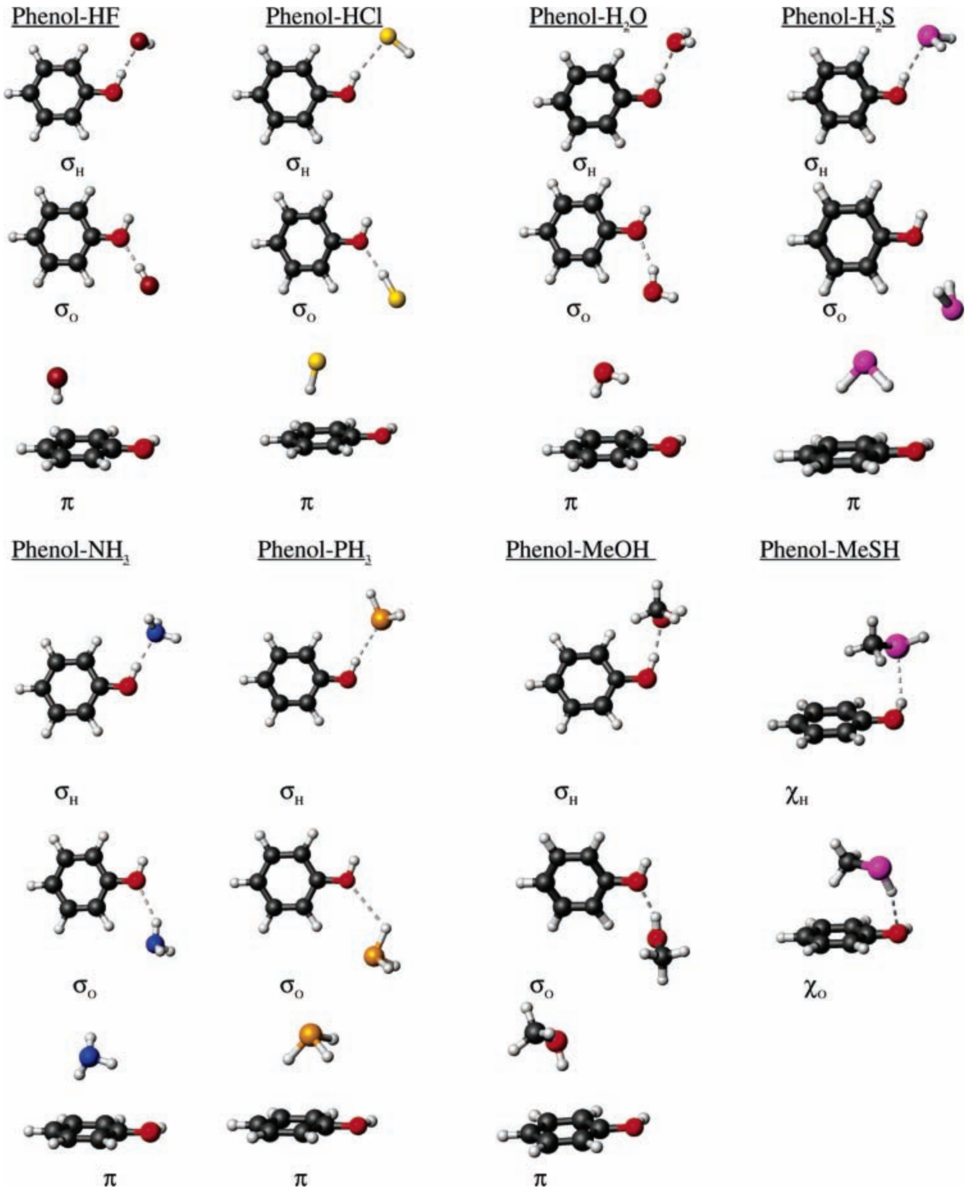

Figure 1. Structures of the hydrogen-bonded complexes of phenol (top view for σ and side view for π conformers).

unsuitable for experiments. In environmental science removal of toxic H_2S is a challenging task, and this subject needs better understanding of its host−guest interaction. Furthermore, no studies on interactions of phenol with H_2S, PH_3, HF, and MeSH are available yet. In addition, comparison of interactions of phenol vis-à-vis water with various solvent/solute molecules would be of importance in consideration of the similarities and dissimilarities between phenol and water.

In this regard, we investigated the nature of interactions of phenol with the first hydrides (HF, H_2O, NH_3), the second hydrides (HCl, H_2S, PH_3), and the analogues of H_2O and H_2S (MeOH, MeSH). These interactions have been studied using reliable ab initio calculations with large basis sets. Here, we differentiate σ complexes of phenol−Y/water−Y into σ_H complex, where interaction is with phenol−H/water−H, and σ_O complex, where the interaction is with phenol−O/water−O. In addition, we find that phenol can also involve in π−H interaction (to be denoted as π-type) and both π−H and σ (σ_H/σ_O) interactions (to be denoted as χ-type (χ_H/χ_O)). We made efforts to investigate the π-conformers as well the difference between σ_H and σ_O conformations. We compared the conformational energetics depending on σ_H-, σ_O-, π-, χ_H-, and χ_O-type interactions and analyzed their energy components (electrostatic, induction, dispersion, and exchange repulsion energies). In addition, by studying the corresponding water−Y complexes, we compare them with phenol−Y complexes.

Computational Details

A comprehensive conformation search was performed in order to ensure adequate sampling of the complex potential-energy surface utilizing our experience with the study of complexes with an aromatic compound. The interaction energies of hydrogen-bonded complexes were calculated by a supermolecular method with second-order Møller−Plesset perturbation theory (MP2) using both the 6-31+G* basis set and the aug-cc-pVDZ (to be shortened as aVDZ) basis sets for full geometry optimization and frequency analysis. All calculations were carried out using the Gaussian03 suite of programs.[21] Most of the figures presented here were drawn using the Pohang Sci-Tech Molecular Modeling (POSMOL).[22]

Symmetry-adapted perturbation theory (SAPT) calculations[23] with a 6-31+G* basis set on the MP2/6-31+G* geometries were performed to analyze the components of interaction energies.

TABLE 1: Binding Energies, SAPT Interaction Energies, and Selected Distances of the Phenol−Y Complexes (Y = HF, H_2O, NH_3, MeOH) at the MP2/6-31+G* [MP2/aug-cc-pVDZ] {MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ} Levels[a]

	phenol−HF			phenol−H_2O		
	σ_H	σ_O	π	σ_H	σ_O	π
ΔE_e	−4.02 ± 0.71	−8.67 ± 1.25	−4.67 ± 1.11	−7.88 ± 1.49	−5.20 ± 1.11	−3.60 ± 1.28
	[−3.79 ± 0.56]	[−7.56 ± 0.80]	[−5.25 ± 1.12]	[−7.02 ± 0.82]	[−4.71 ± 0.74]	[−4.15 ± 1.17]
	{−3.99 ± 0.60}	{−8.08 ± 0.78}	{−5.70 ± 1.04}	{−7.32 ± 0.74}	{−5.05 ± 0.73}	{−4.48 ± 1.03}
ΔE_0	−2.71 [−2.69]	−6.59 [−5.87]	−3.21 [−4.04]	−5.74 [−5.28]	−3.31 [−3.28]	−2.25 [−3.11]
	{−2.47}	{−6.39}	{−4.06}	{−5.58}	{−3.63}	{−3.44}
ΔH_{298}	−2.71 [−2.62]	−7.59 [−6.82]	−3.41 [−4.18]	−5.96 [−5.34]	−3.46 [−3.24]	−2.07 [−2.75]
	{−2.82}	{−7.34}	{−4.62}	{−5.64}	{−3.58}	{−3.08}
E_{elst}	−6.14	−12.93	−4.70	−12.44	−8.83	−3.52
E_{ind}	−1.79	−5.88	−3.85	−4.32	−2.88	−1.28
E_{disp}	−1.33	−2.33	−2.08	−2.49	−2.24	−2.11
E_{exch}	5.52	16.12	8.05	14.63	10.86	4.80
d_{HB}	1.981[1.971]	1.736 [1.720]	2.405 [2.349]	1.869 [1.863]	1.995 [2.004]	2.505 [2.371]
ϕ	162.1 [171.3]	177.1 [173.8]	155.5 [155.9]	177.8 [176.6]	156.6 [156.3]	147.3 [148.8]
Δd_{AH}	0.003 [0.002]	0.013 [0.015]	0.006 [0.008]	0.008 [0.009]	0.006 [0.005]	0.003 [0.004]
μ	2.86 [2.79]	4.49 [4.00]	2.92 [2.87]	4.12 [3.83]	3.37 [2.70]	2.52 [2.29]
q_{CT}	0.013 [0.016]	−0.029 [−0.021]	−0.011 [−0.010]	0.029 [0.032]	−0.011[−0.004]	−0.002 [−0.006]

	phenol−NH_3			phenol−MeOH		
	σ_H	σ_O	π	σ_H	σ_O	π
ΔE_e	−9.82 ± 1.64	−3.70 ± 1.06	−3.49 ± 0.02	−8.89 ± 1.73	−5.55 ± 1.34	−3.87 ± 1.29
	[−9.28 ± 1.07]	[−3.29 ± 1.08]	[−3.33 ± 1.25]	[−8.66 ± 1.39]	[−5.44 ± 1.04]	[−5.95 ± 1.94]
	{−9.56 ± 0.79}	{−3.77 ± 0.69}	{−3.59 ± 1.08}	{−9.00 ± 1.18}	{−5.83 ± 1.01}	{−6.36 ± 1.62}
ΔE_0	−8.06 [−7.44]	−2.35 [−2.11]	−2.44 [−2.57]	−7.01 [−7.15]	−4.28 [−4.45]	−3.15 [−5.02]
	{−7.20}	{−2.59}	{−2.83}	{−7.49}	{−4.84}	{−5.42}
ΔH_{298}	−8.61 [−7.56]	−2.21 [−1.87]	−2.08 [−2.58]	−8.70 [−7.01]	−5.25 [−4.61]	−4.38 [−4.57]
	{−7.84}	{−2.34}	{−2.84}	{−7.35}	{−5.00}	{−4.97}
E_{elst}	−17.59	−6.39	−2.23	−14.37	−8.87	−4.13
E_{ind}	−7.83	−1.84	−0.88	−5.55	−2.95	−2.34
E_{disp}	−3.37	−2.24	−2.28	−3.95	−2.91	−2.82
E_{exch}	23.18	8.25	4.19	18.68	11.54	7.32
d_{HB}	1.875 [1.842]	2.254 [2.271]	2.725 [2.371]	1.840 [1.831]	1.981 [2.013]	2.716 [2.278]
ϕ	171.9 [171.7]	150.5 [151.3]	140.9 [168.4]	165.4 [160.8]	160.2 [155.8]	166.8 [155.0]
Δd_{AH}	0.018 [0.021]	0.003 [0.002]	0.002 [0.000]	0.018 [0.012]	0.004 [0.004]	0.002 [0.003]
μ	4.30 [4.11]	2.19 [2.00]	3.08 [2.52]	3.94[3.40]	3.39 [3.19]	1.39 [1.89]
q_{CT}	0.039 [0.062]	0.005 [0.006]	−0.001 [−0.006]	0.033[0.035]	−0.010 [−003]	−0.005 [−0.007]

[a] All energies are in kcal/mol; distances are in Å; angles in degrees. ΔE_e is the median of the BSSE-corrected and -uncorrected values which can be considered as the upper and lower bounds for the interaction energy, respectively, and the value after ± is one-half the BSSE. ΔE_0 is the ZPVE-corrected ΔE_e. ΔH_{298} is the one-half BSSE-corrected binding enthalpy at 298.15 K and 1.0 atm. E_{int} is the SAPT interaction energy. d_{HB} is the hydrogen-bond distance between H and B atom, Δd_{AH} is the elongation in A−H bond, and ϕ is the angle ∠A−H••B of A−H••B interaction. For π/χ conformers with A−H•• π interaction, d_{HB} is the distance between the ring center to the H atom. μ is the dipole moment in debye. q_{CT} (in au) is the amount of charge transfer from phenol to Y.

The basis set superposition error (BSSE) was investigated. As previously experienced, full BSSE correction tends to underestimate binding energies unless large basis sets are used to take into account most of electron correlation energy. Thus, we report half-BSSE-corrected binding energies ($-\Delta E_e$) so that we obtain realistic binding energies.[4h,20,25] The zero point energy (ZPE) corrected binding energies ($-\Delta E_0$) and enthalpies at room temperature and 1 atm (ΔH_{298}) were also computed. We further carried out MP2 calculations using aug-cc-pVTZ (shortened as MP2/aVTZ) on the MP2/aVDZ geometries. The SAPT interaction energy (E_{int}) has been analyzed up to the second-order symmetry-adapted perturbation theory: the electrostatic energy (E_{elst}) consisting of $E_{elst}^{(10)}$ and $E_{elst,resp}^{(12)}$, induction (E_{ind}) which equals $E_{ind,resp}^{(20)}$, dispersion (E_{disp}) which equals $E_{disp}^{(20)}$, and exchange repulsion (E_{exch}) which equals $E_{exch}^{(10)} + E_{exch}^{(11)} + E_{exch}^{(12)} + E_{exch-ind,resp}^{(20)} + E_{exch-disp}^{(20)}$. The superscripts ($n_1n_2$) denote orders in perturbation theory with respect to intermolecular and intramolecular interaction operators, respectively. The subscript “resp” indicates the term including coupled-perturbed HF response. One distinct advantage of SAPT over the supermolecular approach is that each term in the perturbation series can be physically interpreted.

Results and Discussion

The phenol−Y complexes can make a conventional H-bond (in σ-conformers; σ_H, σ_O), π H-bonds (in π-conformers), and χ H-bonds (χ_H, χ_O). All types of dimeric complexes are shown in Figure 1. Tables 1 (Y = HF, H_2O, NH_3, MeOH) and 2 (Y = HCl, H_2S, PH_3, MeSH) list the binding energies, interaction energy components, and selected geometrical parameters of phenol−Y complexes. These will be compared with water−Y complexes later (Figure 2, Table 3). All optimized phenol−Y complexes at the MP2/6-31+G* and MP2/aVDZ levels are minimum energy structures possessing no imaginary frequency, as confirmed by vibrational frequency calculations.

In the following sections we will discuss the binding energies based on the MP2/aVTZ//MP2/aVDZ results, which take into account dispersion interaction properly, and the optimized geometries and electronic properties (charges and dipole moments) based on MP2/aVDZ results, unless otherwise stated. The frequencies are reported in MP2/6-31+G*[MP2/aVDZ] values. As to relative binding energies, MP2/6-31+G* [MP2/aVDZ] results are in some cases different from MP2/aVTZ results. In such cases the former results are less reliable because of insufficient electron correlation correction due to the small

TABLE 2: Binding Energies, SAPT Interaction Energies, and Selected Distances of the Phenol−Y Complexes (Y = HCl, H_2S, PH_3, MeSH) at MP2/6-31+G* [MP2/aug-cc-pVDZ] {MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ}[a]

	phenol−HCl			phenol−H_2S		
	σ_H	σ_O	π	σ_H	σ_O	π
ΔE_e	−2.53 ± 0.97 [−2.89 ± 0.81] {−3.23 ± 0.76}	−5.54 ± 1.29 [−5.19 ± 1.29] {−6.08 ± 1.13}	−4.18 ± 1.67 [−5.64 ± 1.44] {−6.36 ± 1.52}	−4.35 ± 1.35 [−4.82 ± 1.10] {−5.15 ± 1.05}	−3.94 ± 0.72 [−3.46 ± 0.89] {−4.11 ± 0.68}	−3.73 ± 1.82 [−4.85 ± 1.47] {−5.34 ± 1.35}
ΔE_0	−1.76 [−2.20] {−2.11}	−4.42 [−3.97] {−4.44}	−2.98 [−4.73] {−5.02}	−2.97 [−3.62] {−3.94}	−2.71 [−2.43] {−3.08}	−2.61 [−3.84] {−4.33}
ΔH_{298}	−2.03 [−2.44] {−2.78}	−5.07 [−4.71] {−5.60}	−2.95 [−4.62] {−5.34}	−2.80 [−3.39] {−3.71}	−2.47 [−2.11] {−2.76}	−2.89 [−3.54] {−4.03}
E_{elst}	−3.37	−9.31	−4.05	−6.56	−4.07	−3.60
E_{ind}	−1.75	−3.86	−2.16	−3.78	−1.28	−1.86
E_{disp}	−1.30	−2.67	−3.21	−2.15	−2.00	−3.43
E_{exch}	5.41	13.33	7.42	10.65	5.86	6.99
d_{HB}	2.522 [2.446]	1.914[1.877]	2.367[2.241]	1.869 [1.863]	2.719 [2.205]	3.149[2.312]
ϕ	170.0 [170.0]	174.5[172.3]	153.6[155.8]	177.8 [176.6]	109.3 [164.6]	130.6 [166.7]
Δd_{AH}	0.002 [0.000]	0.013 [0.014]	0.006 [0.009]	0.005 [0.007]	0.001 [0.003]	0.002 [0.003]
μ	1.54 [1.72]	3.89 [3.61]	2.28 [2.36]	2.34 [2.11]	3.08 [2.55]	1.93 [1.92]
q_{CT}	0.018 [0.018]	−0.023 [−0.027]	−0.006 [−0.014]	0.033 [0.036]	0.007 [−0.003]	0.003 [−0.005]

	phenol−PH_3			phenol−MeSH	
	σ_H	σ_O	π	χ_H	χ_O
ΔE_e	−4.19 ± 1.20 [−4.27 ± 1.03] {−4.58 ± 0.95}	−1.69 ± 0.95 [−1.91 ± 0.71] {−2.10 ± 0.73}	−2.20 ± 1.46 [−4.18 ± 1.41] {−4.70 ± 1.34}	−5.92 ± 1.91 [−7.55 ± 2.36] {−8.04 ± 2.02}	−4.27 ± 2.00 [−6.16 ± 2.21] {−6.59 ± 1.97}
ΔE_0	−2.94 [−3.18] {−3.49}	−1.18 [−1.44] {−1.63}	−1.49 [−3.14] {−3.66}	−4.68 [−6.45] {−6.93}	−3.22 [−5.17] {−5.54}
ΔH_{298}	−2.66 [−2.82] {−3.14}	−1.03 [−1.24] {−1.43}	−0.97 [−2.86] {−3.39}	−6.35 [−6.23] {−6.72}	−4.86 [−4.79] {−5.18}
E_{elst}	−6.37	−2.01	−2.11	−9.07	−4.44
E_{ind}	−4.04	−0.78	−1.57	−5.38	−2.17
E_{disp}	−2.31	−1.63	−3.62	−4.90	−4.84
E_{exch}	10.96	3.85	6.23	15.82	7.11
d_{HB}	2.524[2.525]	2.861[2.827]	2.796[2.583]	2.517 [2.499]	2.411 [2.375]
ϕ	170.0[176.5]	117.6[120.4]	135.7[118.3]	140.5 [136.8]	163.1 [166.3]
Δd_{AH}	0.006 [0.006]	−0.003 [−0.002]	0.001 [0.000]	0.003 [0.008]	0.004 [0.003]
μ	2.97 [2.75]	1.69 [1.57]	1.86 [1.95]	2.01[1.97]	3.27 [3.14]
q_{CT}	0.030 [0.028]	0.008 [0.007]	0.002 [−0.006]	0.027 [0.025]	−0.005 [−0.011]

[a] See the footnote of Table 1.

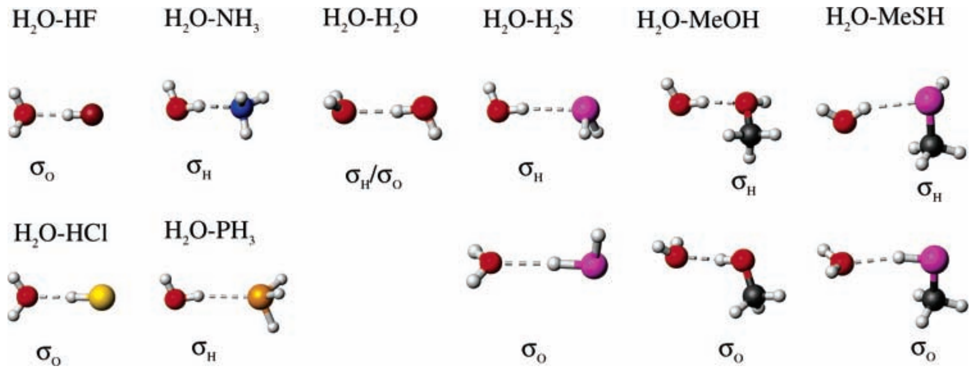

Figure 2. Structures of the hydrogen-bonded dimeric complexes of H_2O.

size of the basis set, and so we assume that MP2/aVTZ results are more reliable.

In the case of the phenol−HF complex the σ_O complex is the most stable isomer. The MP2/aVTZ ZPE-uncorrected binding energies (D_e or $-\Delta E_e$) of σ_H-, σ_O-, and π-type conformers are 3.99, 8.08, and 5.70 kcal/mol, respectively. Their ZPE-corrected binding energies (D_0 or $-\Delta E_0$) are 2.47, 6.39, and 4.06 kcal/mol, respectively. The O···H bond distances (d_{HB}) are 1.971, 1.720, and 2.349 Å, respectively, and the elongations in the distance from the proton acceptor (A) to the hydrogen (Δd_{AH}) are 0.002, 0.015, and 0.008 Å, respectively. Since HF is a stronger proton donor than phenol, the σ_O conformer has the shortest H-bond length and the largest elongation of Δd_{AH} and is the most stable (D_0 = 6.39 kcal/mol), followed by the π conformer, while the σ_H conformer is the least stable. On the basis of the natural bond orbital (NBO) charges [q_O(phenol) = −0.71, q_H(phenol) = 0.49, q_H(HF) = 0.56, q_F(HF) = −0.56 au], the electrostatic energy gain for the σ_O-type interaction between O(phenol) and H(HF) would be larger than that for σ_H-type interaction between F(HF) and H(phenol), which is in agreement with the largest SAPT electrostatic energy gain for the σ_O-type (E_{elst} for σ_H-, σ_O-, and π-types are −6.14, −12.93, and −4.70 kcal/mol, respectively). This maximal electrostatic energy gain by the σ_O-type can also be noted from the large dipole moment (μ) of the σ_O-type phenol−HF complex (arisen from the dipole−dipole interaction between phenol and HF) [μ

TABLE 3: Binding Energies, SAPT Interaction Energies, and Selected Distances of the Water−Y Complexes (Y = HF, H_2O, NH_3, MeOH, HCl, H_2S, PH_3, MeSH) at the MP2/6-31+G* [MP2/aug-cc-pVDZ]{MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ} Levels[a]

	H_2O-HF	H_2O-H_2O	H_2O-NH_3	$H_2O-MeOH$	
	σ_O	σ	σ_H	σ_H	σ_O
ΔE_e	−10.01 ± 1.27 [−8.50 ± 0.64] {−8.88 ± 0.54}	−6.00 ± 1.05 [−4.88 ± 0.46] {−5.17 ± 0.46}	−7.40 ± 1.16 [−6.42 ± 0.62] {−6.71 ± 0.46}	−5.66 ± 0.63 [−9.81 ± 1.39] {−5.95 ± 0.58}	−5.88 ± 1.18 [−4.95 ± 0.52] {−5.23 ± 0.50}
ΔE_0	−7.29 [−5.73] {−6.11}	−3.49[−2.75] {−3.04}	−4.87 [−4.21] {−4.50}	−4.70 [−3.71] {−3.99}	−3.91 [−3.33] {−3.62}
ΔH_{298}	−8.13 [−6.22] {−7.19}	−4.11[−2.03] {−3.51}	−5.46 [−4.66] {−5.55}	−5.05 [−3.41] {−4.28}	−4.07 [−2.77] {−3.65}
E_{elst}	−15.50	−10.10	−13.56	−11.27	−9.94
E_{ind}	−6.21	−3.01	−5.10	−3.80	−3.21
E_{disp}	−1.87	−1.47	−1.95	−1.95	−1.73
E_{exch}	17.59	10.92	16.10	13.22	11.58
d_{HB}	1.736 [1.712]	1.928 [1.945]	1.966 [1.964]	1.890 [1.899]	1.923 [1.935]
ϕ	177.1 [177.8]	174.4 [171.4]	171.3 [170.7]	172.5 [161.4]	178.0 [176.7]
Δd_{AH}	0.016 [0.018]	0.007 [0.007]	0.014 [0.013]	0.009 [0.009]	0.006 [0.006]
μ	4.72 [4.18]	3.23 [2.62]	3.99 [3.55]	3.04 [2.04]	3.21 [2.74]
q_{CT}	−0.036[0.037]	0.019[0.019]	0.032[0.031]	0.024[0.025]	−0.021[−0.021]

	H_2O-HCl	H_2O-H_2S		H_2O-PH_3	$H_2O-MeSH$	
	σ_O	σ_H	σ_O	σ_H	σ_H	σ_O
ΔE_e	−5.71 ± 1.03 [−5.76 ± 0.63] {−6.06 ± 0.75}	−3.25 ± 0.71 [−3.15 ± 0.62] {−3.98 ± 0.61}	−2.90 ± 0.64 [−2.91 ± 0.43] {−3.06 ± 0.43}	−2.79 ± 0.65 [−2.59 ± 0.49] {−2.89 ± 0.51}	−3.99 ± 0.74 [−4.69 ± 0.94] {−4.98 ± 0.74}	−2.85 ± 0.73 [−2.63 ± 0.46] {−2.74 ± 0.41}
ΔE_0	−3.82 [−3.72] {−4.02}	−1.91[−1.55] {−2.38}	−1.30 [−1.58] {−1.73}	−1.23 [−1.27] {−1.57}	−2.50 [−2.86] {−3.16}	−1.81 [−1.63] {−0.92}
ΔH_{298}	−4.95 [−3.90] {−4.80}	−1.86[−1.11] {−2.54}	−1.39 [−0.94] {−1.69}	−1.28 [−0.58] {0.47}	−2.52 [−2.55] {−3.44}	−2.07 [−0.68] {−1.20}
E_{elst}	−10.72	−5.09	−5.87	−4.76	−6.54	−4.96
E_{ind}	−3.98	−2.23	−1.87	−2.39	−2.99	−1.75
E_{disp}	−1.87	−1.02	−1.29	−1.09	−1.64	−1.37
E_{exch}	13.43	6.63	7.18	6.87	8.70	6.78
d_{HB}	1.896[1.847]	2.131 [2.519]	2.131 [2.180]	2.625[2.626]	2.485 [2.425]	2.169
ϕ	178.0 [178.3]	177.4 [164.2]	177.4 [177.6]	170.2[164.8]	151.0 [151.6]	1698
Δd_{AH}	0.0017[0.019]	0.002 [0.005]	0.004 [0.012]	0.004 [0.004]	0.006 [0.007]	0.001
μ	4.45 [3.76]	2.01 [1.33]	3.77 [2.93]	3.08 [2.45]	0.99 [0.72]	3.76 [2.90]
q_{CT}	0.029 [0.041]	0.018 [0.018]	−0.011 [−0.013]	0.016 [0.011]	0.021 [0.022]	−0.010 [−0.012]

[a] See the footnote of Table 1. q_{CT} (in au) is the amount of charge transfer from H_2O to Y.

for the σ_H-, σ_O-, and π-types are 2.79, 4.00, and 2.87 D, respectively]. In addition, due to the charge transfer (q_{CT}) from phenol to the interacting molecule [q_{CT} for σ_H-, σ_O-, and π-types are 0.016, −0.021, −0.010 au, respectively], the induction is maximized also for the σ_O-type.

In the case of phenol−H_2O complex the D_e values of σ_H-, σ_O-, and π-type conformers are 7.32, 5.05, and 4.48 kcal/mol, respectively, and their D_0 values are 5.58, 3.63, and 3.44 kcal/mol, respectively; their d_{HB} values are 1.863, 2.004, and 2.371 Å, respectively, and their Δd_{AH} values are 0.009, 0.005, and 0.004 Å, respectively. Since H_2O is a weaker proton donor than phenol due to its lower acidity, the σ_H conformer has the shortest H-bond length and the largest elongation of Δd_{AH} and is more stable than the σ_O and π conformers. On the basis of the NBO charges of the water molecule [$q_H(H_2O) = 0.48$ and $q_O(H_2O) = -0.97$ au], the electrostatic energy gain by the σ_H-type interaction between $O(H_2O)$ and H(phenol) would be larger than that for σ_O-type interaction between O(phenol) and $H(H_2O)$, which is in agreement with the largest SAPT electrostatic energy gain for the σ_H-type interaction [E_{elst} for σ_H-/σ_O-/π-type = −12.44/−8.83/−3.53 kcal/mol] and the largest dipole moment for the σ_H type [μ for σ_H-/σ_O-/π-type = 3.83/2.70/2.29 D]. As q_{CT} for σ_H-, σ_O-, and π-types are 0.032, −0.004, and −0.006 au, respectively, the electrostatic interaction is maximized for the σ_H-type. The calculated D_0 value for the σ_H minimum (5.58 kcal/mol) is in good agreement with the experimental values[7,24] (5.48 ± 0.09, 5.60 ± 0.11 kcal/mol). This phenol−H_2O binding energy is slightly smaller than the σ_O phenol−HF binding energy (6.39 kcal/mol).

For the phenol−NH_3 system the D_e of σ_H-, σ_O-, and π-type conformers are 9.56, 3.77, and 3.59 kcal/mol, respectively, and their D_0 are 7.20, 2.59, and 2.83 kcal/mol, respectively; their d_{HB} values are 1.842, 2.271, and 2.371 Å, respectively, and their Δd_{AH} values are 0.021, 0.002, and 0.000 Å, respectively. Since NH_3, being a stronger base, is a stronger proton acceptor than phenol, the σ_H conformer has the shortest H-bond length and the largest elongation of Δd_{AH} and is more stable than the σ_O and π conformers. The D_0 value for σ_H phenol−NH_3 (7.20 kcal/mol) is much larger than those of σ_O phenol−HF and σ_H phenol−H_2O. This is also clearly understood from the fact that the σ_H conformer has the largest E_{elst} (σ_H-/σ_O-/π-type = −12.44/−8.83/−3.53 kcal/mol), largest μ (σ_H-/σ_O-/π-type = 3.83/2.70/2.29 D), and largest q_{CT} (σ_H-/σ_O-/π-type = 0.032/−0.004/−0.006 au).

In the case of phenol−MeOH complex the D_e of σ_H-, σ_O-, and π-type conformers are 9.00, 5.83, and 6.36 kcal/mol, respectively, their D_0 are 7.49, 4.84, and 5.42 kcal/mol, their Δd_{AH} values are 0.012, 0.004, and 0.003 Å, and their q_{CT} are 0.035, −0.003, and −0.007 au, respectively. As $q_O(MeOH) = -0.77$ au and $q_H(MeOH) = 0.47$ au, MeOH is a weaker proton donor than phenol. Thus, the σ_H conformer has the shortest H-bond length and the largest elongation of Δd_{AH} and is more stable than the σ_O and π conformers. Again, this can be understood from the large electrostatic energy gain, large dipole

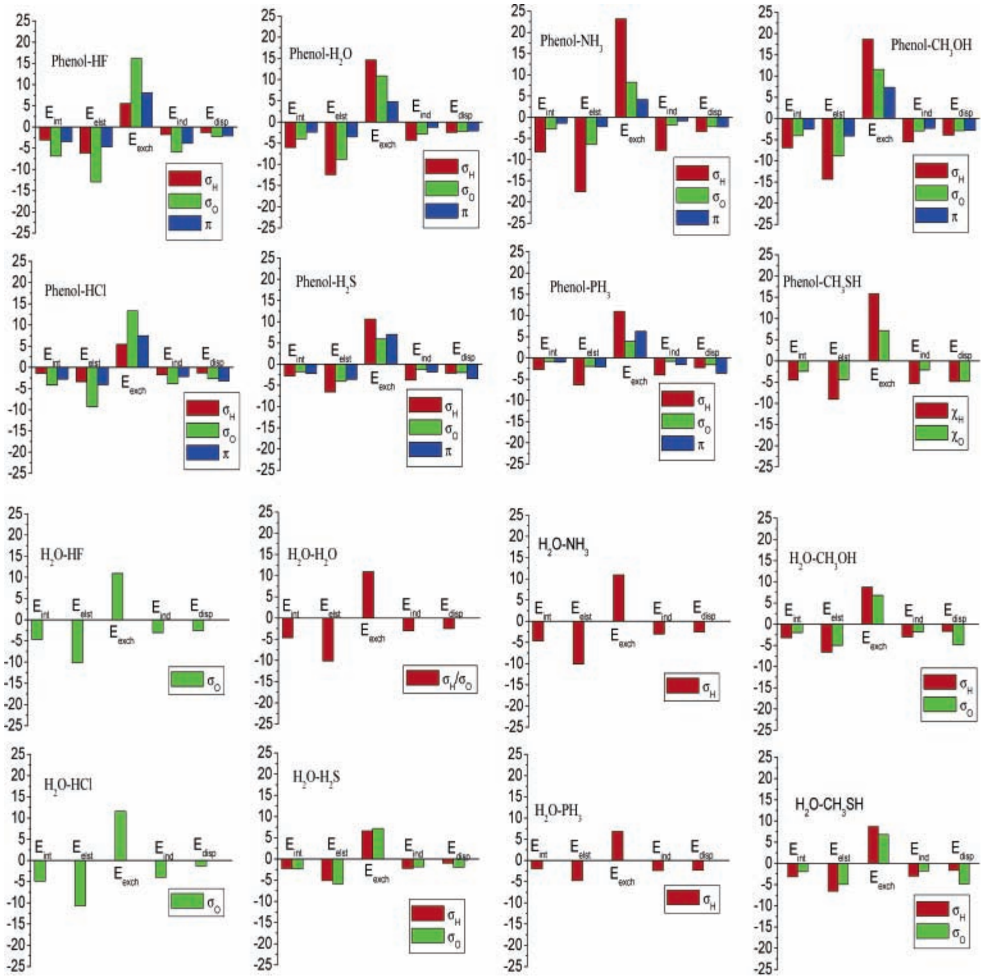

Figure 3. Bar plots of SAPT interaction energy (E_{int}) and its components (E_{elst}, E_{ind}, E_{disp}, E_{exch}; MP2/6-31+G*) for the various conformers of phenol−Y and H_2O−Y complexes [Y = HF, NH_3, H_2O, MeOH, HCl, PH_3, H_2S, MeSH]. All the vertical axes represent energy in kcal/mol.

moment, and large charge transfer for the σ_H conformer. The D_0 value for σ_H phenol−MeOH (7.49 kcal/mol) is larger than that of the σ_H phenol−H_2O conformer (5.58 kcal/mol). In the case of π conformers we located only the structure involving in $\pi\cdots$HO(MeOH) interaction but not $\pi\cdots$HC(MeOH) interaction with which no stable minimum energy conformer was found. The stability of the most stable conformers in terms of D_0 decreases in the following order phenol−MeOH (σ_H) ≈ phenol−NH_3 (σ_H) > phenol−HF (σ_O) > phenol−H_2O (σ_H).

The relative stability of the phenol complexes for the first-row hydrides and MeOH is guided mainly by electrostatic interactions. On the other hand, the interactions of phenol with the second-row hydrides and MeSH are different from those with the first hydride systems because of weaker electrostatic interactions but stronger dispersion energies, as shown in Table 2.

In the case of phenol−HCl complex the D_e of σ_H-, σ_O-, and π-type conformers are 3.23, 6.08, and 6.36 kcal/mol, respectively, and their D_0 are 2.11, 4.44, and 5.02 kcal/mol, respectively. The π conformer is the most stable followed by the σ_O conformer, and the σ_H conformer is the least stable. The dispersion energy gain (E_{disp}) by the π-type interaction is large, as seen from the SAPT calculation.

The results for the σ_H conformer of phenol−H_2S/NH_3 are different from those of phenol−H_2O/PH_3 as sulfur/phosphorous is less electronegative than oxygen/nitrogen, thus making the H-bond weaker. The D_0 of σ_H-, σ_O-, and π-type conformers of phenol−H_2S/phenol−PH_3 are 3.94/3.49, 3.08/1.63, and 4.33/3.66 kcal/mol, respectively. The π conformer is the most stable with large dispersion energy gain followed by the σ_H conformer, and the σ_O conformer is the least stable.

In contrast to phenol−MeOH, phenol−MeSH has stronger dispersion interaction, resulting in stronger π−H interaction. Therefore, this system involves in χ-type H-bonding which includes both σ and π H-bonds. The χ_H interaction (D_0 = 6.93 kcal/mol) is stronger than the χ_O interaction (D_0 = 5.54 kcal/mol) because the σ_H interaction is stronger than the σ_O interaction in this case.

In going from HF to H_2O to NH_3 the σ_H binding energy "D_0" increases from 2.5 to 5.6 to 7.2 kcal/mol, the σ_O binding energy decreases from 6.4 to 3.6 to 2.6 kcal/mol, and the π-binding energy decreases from 4.1 to 3.4 to 2.8 kcal/mol. Although MeOH can be considered to be similar to H_2O, the phenol−MeOH binding energy (σ_H = 7.5, σ_O = 4.8, π = 5.4 kcal/mol) is much larger than the phenol−H_2O energy due to the extra dispersion energy for the π−H interaction by the Me group. For the second-row hydrides from HCl to H_2S to PH_3 the σ_H binding energy increases (2.1, 3.9, 3.5 kcal/mol) while the σ_O binding energy decreases (4.4, 3.1, 1.6 kcal/mol) and the π-binding energy also decreases (5.0, 4.3, 3.7 kcal/mol). In the case of MeSH the χ_H and χ_O binding energies (6.9 and 5.5 kcal/mol) are large due to large dispersion energies. In the cases of the first hydrides the σ_O complex of HF is ca. 4 kcal/mol more stable than the σ_H conformer, while the σ_H conformers of H_2O and NH_3 are more stable than the corresponding σ_O ones by ca. 2 and 5 kcal/mol, respectively. On the other hand, in the

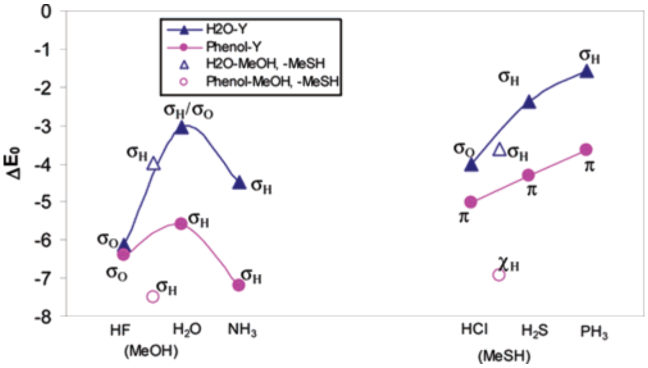

Figure 4. Interaction energies (ΔE_0; MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ) for phenol−Y and H_2O−Y [Y = HF, NH_3, H_2O, MeOH, HCl, PH_3, H_2S, MeSH].

second hydride systems the π complexes are slightly more stable (by only a fraction of 1 kcal/mol) than, but compete with, the σ_O complex for HCl and the σ_H complexes for H_2S and PH_3. The H-bonding types of the global minimum energy structures are σ_O for HF, σ_H for H_2O, NH_3, PH_3, and MeOH, π for HCl, H_2S, and PH_3, and χ_H for MeSH. In the phenol−Y clusters the SAPT interaction energies E_{int} are dominated by attractive electrostatic and repulsive exchange energies. However, in the case of π complexes where the electrostatic and exchange interactions are weaker, the dispersion and induction energies become important among the interaction energy components. As seen in Figure 3 and Tables 1−3 which include phenol−Y (and water−Y to be discussed below) E_{int} is correlated with E_{ind}, while it is hard to find a good correlation between E_{int} and $E_{elst}/E_{disp}/E_{exch}$. This is because the sum of E_{elst} and E_{disp} tends to cancel out E_{exch}. It is partially related with the trend that not only is E_{disp} already well correlated with E_{exch}, but also the main interaction E_{elst} needs to be balanced by E_{exch}.

It is interesting to compare the phenol−Y system with the water−Y system. The minimum energy conformers of the latter system are shown in Figure 2, and the relevant energies and selected geometries are compiled in Table 3. For the lowest energy conformers of water−Y complexes the binding energies (D_0) for HF (σ_O), H_2O (σ_H/σ_O), $NH_3(\sigma_H)$, and MeOH (σ_H) are 6.11, 3.04, 4.50, and 4.32 kcal/mol, respectively, which are compared with the corresponding phenol−Y binding energies (6.39, 5.58, 7.20, and 7.49 kcal/mol, respectively; Figure 4). In the case of water dimer the σ-type includes both σ_H and σ_O types. As q_O(phenol) = −0.71 au and q_O(water) = −0.97 au, the O atom of water is better stabilized by accepting an H atom than the O atom of phenol. Thus, the σ_O bonding is likely to enhance water−Y interactions more than phenol−Y interactions, while the σ_H bonding is likely to enhance water−Y interactions less than phenol−Y interactions. Indeed, the σ_H bonding enhances stabilization of phenol−Y (D_0 = 2.47/5.58/7.20/7.49 kcal/mol for Y = HF/H_2O/NH_3/MeOH) more than water−Y (D_0 = −/3.04/4.50/4.32 kcal/mol; the σ_H for water−HF is not the local minimum), and the binding energy differences between the two systems are large. On the other hand, the σ_O bonding enhances stabilization of water−Y (D_0 = 6.11/3.04/-/3.62 kcal/mol; the σ_O for water−NH_3 is not the local minimum) more than phenol−Y (D_0 = 6.39/3.63/2.59/4.84 kcal/mol), and thus the binding energy differences between the two systems are drastically reduced.

For the second row hydrides, the binding energies (D_0) of a water molecule interacting with HCl (σ_O), H_2S (σ_H), $PH_3(\sigma_H)$, and MeSH (σ_H) are 4.02, 2.38, 1.57, and 3.16 kcal/mol, respectively, which are smaller than the phenol−Y binding energies of π and χ_H complexes (5.02, 4.33, 3.66, and 6.93 kcal/mol, respectively; Tables 2 and 3, Figure 4). Therefore, due to the strong dispersion energy components by the π−H interaction, a phenol molecule interacts with the second hydride systems more strongly than a water molecule does, which can be noted from Figures 3 and 4.

As vibrational spectroscopy is an indispensable tool for successful identification and characterization of H-bonds,[26] we studied the phenolic O−H stretch and the intermolecular stretch which are highly sensitive to the molecular environment by

TABLE 4: Calculated and Experimental Vibrational Frequency Shifts (cm^{-1}) of Phenolic O−H Stretch ($\delta\nu_{OH}$) and Intermolecular Stretch Modes (ν_{int}) for Phenol−Y Complexes at the MP2/6-31+G* [MP2/aug-cc-pVDZ] Levels. $I^r\nu_{OH}$ Is the Intensity Ratio of the Complexed Phenol to the Uncomplexed One for the ν_{OH} Mode[a]

	phenol−HF			phenol−HCl		
	σ_H	σ_O	π	σ_H	σ_O	π
$\delta\nu_{OH}$	−2 [−35]	12 [7]	−1 [−3]	−15 [−44]	1[−4]	0 [−3]
$I^r\nu_{OH}$	4.4 [4.9]	1.5 [1.4]	1.2 [1.2]	4.4 [5.0]	1.2 [1.2]	1.1 [1.1]
ν_{int}	125 [113]	187 [178]	115 [125]	81[84]	118[115]	81 [95]

	phenol−H_2O				phenol−H_2S		
	σ_H	σ_O	π	expt	σ_H	σ_O	π
$\delta\nu_{OH}$	−120[−173]	4 [1]	2 [1]	−132	−90 [−138]	−4 [−7]	−3 [−7]
$I^r\nu_{OH}$	10.1 [10.4]	1.1 [1.0]	1.1 [1.1]		8.8 [9.5]	1.0 [1.0]	1.1 [1.1]
ν_{int}	177 [157]	150[131]	102 [99]	155	98 [102]	84 [88]	74 [92]

	phenol−NH_3				phenol−PH_3		
	σ_H	σ_O	π	expt	σ_H	σ_O	π
$\delta\nu_{OH}$	−340[−419]	3 [−3]	0 [−2]	−362	−104[−125]	−2 [−4]	0 [−5]
$I^r\nu_{OH}$	18.6 [19.6]	0.9 [0.9]	1.0 [1.0]		8.7 [8.7]	0.9 [0.9]	1.0 [0.9]
ν_{int}	198 [190]	119 [118]	90 [122]	164	92 [92]	58 [62]	67 [86]

	phenol−MeOH				phenol−MeSH	
	σ_H	σ_O	π	expt	χ_H	χ_O
$\delta\nu_{OH}$	−171[−232]	6 [−3]	−2 [−6]	−201	−105 [−142]	−7 [−10]
$I^r\nu_{OH}$	10.5 [9.8]	1.2 [1.1]	1.1 [1.1]		4.5 [3.7]	1.0 [1.0]
ν_{int}	190 [179]	150 [134]	108 [118]	162	111 [119]	82 [94]

[a] Experimental data are from refs 6, 15, 27, and 28.

virtue of specific (H-bonding) and nonspecific interactions. To correct the overestimation of harmonic frequencies, a single scale factor of 0.96 was used to scale all frequencies. Henceforth, the scaled frequencies are discussed unless otherwise stated. It should be noted in Table 4 that the OH stretch mode of phenol (ν_{OH}) as the proton donor (σ_H conformers) undergoes a drastic red shift along with sharply increased intensity while those of phenol as the proton acceptor (σ_O conformers) and π conformers hardly change. The small red shifts for phenolic O−H stretch in the case of phenol−HF and phenol−HCl complexes (in comparison with other phenol−Y heterodimers) can be understood from the weak basicity of HF/HCl monomers. The red shifts which are proportional to H-bond strengths tend to follow the basicity order of the interacting molecule Y.

The MP2/6-31+G* [MP2/aVDZ] intermolecular stretching frequencies (ν_{int}) for the σ_H complexes of phenol interacting with H_2O, NH_3, and MeOH are predicted to be 183[163], 198[190], and 198[187] cm^{-1}, respectively, which agree well with the corresponding observed values[6,15,17,27] 155, 164, and 162 cm^{-1}. The red shift of the phenolic O−H stretching frequency relative to that of bare phenol ($-\delta\nu_{OH}$) is well correlated with the O−H bond elongation upon H-bond formation in σ_H complexes. The predicted red shifts $-\delta\nu_{OH}$ for the above three σ_H complexes (120[173], 340[419], and 171[232] cm^{-1}, respectively) compare well with the corresponding experimental values[6,15,17,27] (132, 362, and 201 cm^{-1}, respectively). It should also be noted that the intensity ratio is 10−20-fold for the first-row hydride and MeOH and 5−10-fold for the second-row hydrides and MeSH. This drastic enhancement in intensity was already proven in experiments of phenol with H_2O and NH_3.[28] It is very clear that for H_2O, NH_3, and MeOH only the σ_H conformers which are the lowest energy structures can explain the observed characteristic spectra since their σ_O and π conformers hardly show frequency shifts and intensity changes in the calculations. As our calculated results are in good agreement with the available experimental data, we predict that the lowest energy conformers of σ_O phenol−HF and π phenol−HCl/H_2S/PH_3/MeSH would show minimal red shift for $-\delta\nu_{OH}$. In addition, the intermolecular stretching frequency ν_{int} for σ_O phenol−HF is predicted to be 187[178] cm^{-1}, those for π phenol−HCl/H_2S/PH_3 are predicted to be 81[95], 74[92], and 67[86] cm^{-1}, respectively, and that for the χ_H phenol−MeSH is 111[119] cm^{-1}.

Finally, only in the case of the σ_O phenol−PH_3 among all the phenol−Y conformers studied here we note that the P−H bond (Δd_{AH}) undergoes shortening, resulting in a blue shift by 13[15] cm^{-1}. This is due to the van der Waals interaction of P and O atoms as indicated by their distance (3.753 Å at MP2/aVDZ) and the P···HC interaction. In the case of NH_3 as a proton acceptor in the σ_H phenol−NH_3 complex the characteristic intense symmetric NH_3 bending mode (umbrella motion) responsible for charge-transfer undergoes a remarkable red shift by 103 [85] cm^{-1}.

Concluding Remarks

The nature and origin of interactions in neutral σ (σ_H, σ_O), π, and χ(χ_H, χ_O) complexes of phenol with a solvent/solute molecule (HF, HCl, H_2O, H_2S, NH_3, PH_3, MeOH, and MeSH) were studied using MP2 calculations with 6-31+G*, aug-cc-pVDZ, and aug-cc-pVTZ basis sets. The structures, binding energies, dipole moments, charge-transfer, vibrational spectra, and IR intensity, thermochemical properties, and interaction energy components were investigated and compared with any available experimental results. The structures, binding energies, and spectra of phenol interacting with HF, HCl, H_2S, PH_3, and MeSH are first reported here, which would help facilitate experimental studies. The guiding principle for forming the most stable complex is elucidated from the present study. The H-bond length change, charge, charge transfer, and dipole moment are well correlated with the electrostatic energy gain for the σ complexation. The dispersion energy plays an important role in π complexes of phenol interacting with the second hydrides. The comparison of interactions of phenol vis-à-vis water with various solvent/solute molecules would be of importance in consideration of the similarities and dissimilarities between phenol and water.

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