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How Well Can Density Functional Methods Describe Hydrogen Bonds to π Acceptors?

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Abstract

We employed four newly developed DFT methods for the calculation of five π-hydrogen bonding systems, namely, H_2O-C_6H_6, NH_3-C_6H_6, HCl-C_6H_6, H_2O-indole and H_2O-methylindole. We report new coupled cluster calculations for HCl-C_6H_6 that support the experimental results of Gotch and Zwier. Using the best available theoretical and experimental results for all five systems, our calculations show that the recently proposed MPW1B95, MPWB1K, PW6B95, and PWB6K methods give accurate energetic and geometrical predictions for π hydrogen bonding interactions, for which B3LYP fails and PW91 is less accurate. We recommend the most recent DFT method, PWB6K, for investigating larger π-hydrogen bonded systems, such as occur in molecular recognition, protein folding, and crystal packing.

1. Introduction

Hydrogen bonds in which the acceptor (base) is an aromatic π system differ in qualitative ways from conventional hydrogen bonds.[1-14] The special case in which water is the donor (acid) is of great practical importance in solvation, hydrophobic interactions, molecular recognition, protein folding, neurotransmitter conformations, crystal packing, and cluster and micelle formation. More generally, π hydrogen bond acceptors are important for drug design, crystal engineering, and supramolecular chemistry and as precursor complexes in reaction mechanisms.[15-22] Due to their physical, chemical, and biological importance, the interactions of hydrogen bond donors with benzene and with indole and its derivatives have been extensively studied both experimentally[1-3,5-10,13-34] and theoretically.[4,7,11,12,28,35-44] Correlated ab initio methods such as second-order Møller-Plesset perturbation theory (MP2)[45,46] are capable of describing this kind of π acceptor hydrogen bonding.[7,36-39,43,47] For example, Niu and Hall concluded:[17] "DFT calculations underestimate this α- agostic interaction between CpRh(CO) and CH_4. Other work on the binding of alkanes to tungsten pentacarbonyl, alkane-$W(CO)_5$, also shows that the conventional ab initio methods give an excellent description of these weak bonding energies, especially in the larger basis sets. The problem here, of course, is that current functionals do not correctly describe the dispersion energy, which is well described by MP2 calculations." It is well recognized that DFT does not give the correct long-range inverse sixth power law for dispersion because it predicts no interaction at distances where there is no overlap of spherically symmetric interacting particles, but it would be an oversimplification to dismiss DFT methods for noncovalent interaction in general. For example, hydrogen bonding involves not only dispersion but also electrostatic interactions, polarization (induction), and charge transfer.[48,49] Furthermore, it should be recognized that the dispersion-like interactions that contribute to hydrogen bonding involve much shorter internuclear distances than those where the interaction is dominated by overlap-free dispersion.[50] Among hydrogen bond types, there is a smaller relative

contribution for π acceptor than for conventional Lewis bases.[47] Thus these systems provide a theoretical challenge in that they require a balanced description of electrostatic, induction, and dispersion like attractive interactions and exchange repulsion interactions.

Density functional theory (DFT) is very appealing due to its excellent performance-to-cost ratio, and DFT methods are widely employed in the computational chemistry community. However, the most popular DFT method, B3LYP,[51,52] cannot successfully describe π hydrogen bonding[37,43] and B3LYP also fails badly for binding energies dominated by dispersion interactions,[53-55] even though the equilibrium geometries of complexes occur in a region where repulsive interactions are important. During the last decade, DFT methods have been greatly improved, but we did not find any DFT studies that give satisfactory results for π facial hydrogen bonding in which an aromatic ring is the hydrogen bond acceptor. In the present paper, we test whether the new DFT methods developed by our group, namely MPW1B95,[54] MPWB1K,[54] PW6B95,[56] and PWB6K,[56] are suitable for describing this type of O-H···π hydrogen bonding. This is an interesting question because these new DFT methods have previously been shown to have good performance for a wider range of bonding and noncovalent interactions than previous density functionals,[54,56] but no π acceptor hydrogen bonds were considered during their development, nor have they previously been tested for this kind of interaction. The new density functionals are all based on the Becke95[57] correlation functional, which includes kinetic energy density, and they have exchange functionals that, in conjunction with the correlation functionals, lead to more accurate descriptions of exchange-correlation energy in the large-reduced-density-gradient region than most previous exchange functionals. We have previously shown[54] that the large-reduced-density-gradient region is very important for noncovalent interactions.

The DFT methods and computational details are described in section 2, and results and discussion are given in section 3. Section 4 contains concluding remarks.

2. Computational Methods

In the present study, we consider six complexes, namely, H_2O-C_6H_6, H_2O-indole normal hydrogen bonded complex (H_2O-indole-NH), H_2O-indole π hydrogen bonded complex (H_2O-indole-πA), H_2O-methylindole-πA, NH_3-C_6H_6, and HCl-C_6H_6.

We estimated the CCSD(T) complete basis limit binding energies for the H_2O-C_6H_6, NH_3-C_6H_6, and HCl-C_6H_6 complexes:

$$\Delta E^{CCSD(T)}/CBS = \Delta E^{MP2}\ IB + (\Delta E^{CCSD(T)} - \Delta E^{MP2})_{small\ basis}, \quad (1)$$

where ΔE^{MP2} IB is an infinite basis set calculation that involves the separate extrapolation of Hartree-Fock and correlation energies.[58,59] The Hartree-Fock (HF) energies are extrapolated by

$$E^{HF}(n) = E_{\infty}^{HF} + A^{HF} n^{-\alpha} \quad (2)$$

and the MP2 correlation energies are extrapolated by

$$E^{cor}(n) = E_{\infty}^{cor} + A^{cor} n^{-\beta}, \quad (3)$$

where n represents the highest angular momentum in an augmented correlation-consistent basis set; $n = 2$ for the aug-cc-pVDZ basis, and $n = 3$ for the aug-cc-pVTZ basis. The parameters α and β are determined in a previous paper;[59] the value used for α is 4.93, and that for β is 2.13. We use the DIDZ (which denotes 6-31+G(d,p))[46] basis set for the $(\Delta E^{CCSD(T)} - \Delta E^{MP2})$ term in Eq. (1).

All DFT calculations were carried out using a locally modified *Gaussian03*[60] program. MPW1B95 and PW6B95 are DFT methods designed for thermochemistry, and MPWB1K and PWB6K are DFT methods designed for thermochemical kinetics.[54,56] The density functionals used in these new methods build on the functionals developed previously by Becke,[51,57,61] Perdew and Wang,[62] and Adamo and Barone.[63] The performance of the four methods for other type of properties can be found in our previous papers.[54-56]

Two basis sets are used in the present study: the smaller is DIDZ and the larger is abbreviated as MG3S (which is the same as 6-311+G(2df,2p) [64] for the systems in this

paper, except for Cl, for which MG3S has 3d2f polarization functions and an improved set of contracted Gaussian in the nonpolarization space). For all hydrogen-bonded complexes, we performed calculations with and without counterpoise corrections[65,66] for basis set superposition error (BSSE). Note that the counterpoise-corrected binding energies were calculated at the geometries optimized without counterpoise correction.

3. Results and Discussion

Figure 1 shows the structures of the hydrogen-bonded complexes studied in the present work.

3.1. Benchmark Calculation

Table 1 gives the benchmark results for the interaction energies of the H_2O-C_6H_6, NH_3-C_6H_6, and HCl-C_6H_6 complexes. Table 1 shows that Hartree-Fock (HF) theory cannot describe the π hydrogen bonding, and it gives negative binding energies for the NH_3-C_6H_6 and HCl-C_6H_6 complexes. This confirms that π hydrogen bonding is dominated by electron correlation. Table 1 also shows that MP2/IB calculations overestimate the binding energies of the three π hydrogen bonded complexes. The ($\Delta E^{CCSD(T)}$ - ΔE^{MP2}) correction contributes about 0.7 kcal/mol to the final dissociation energies of the HCl-C_6H_6 complex, which is much greater than its contributions to the H_2O-C_6H_6 and NH_3-C_6H_6 complexes (0.3 kcal/mol). The estimated CCSD(T)/CBS binding energies for the H_2O-C_6H_6 and NH_3-C_6H_6 are in good agreement with the experiments. There is a debate about the experimental binding energies for the HCl-C_6H_6 complexes. In 1985, Walters *et al*.[3] reported a dissociation energy of the HCl-C_6H_6 complex: $D_0 = 4.79 \pm 0.12$ kcal/mol ($D_e \approx 5.8$ kcal/mol). This is in disagreement with the 1992 value obtained by Gotch and Zwier.[8] Gotch and Zwier used the dispersed fuorescence scan approach, and they bracketed the dissociation energy: 1.8 kcal/mol $\leq D_0 \leq$ 3.8 kcal/mol. Adding zero point energy (ZPE) gives 2.83 kcal/mol $\leq D_e \leq$ 4.83 kcal/mol (where ZPE was taken from an ab initio calculation[36]). Our estimated CCSD(T)/CBS

binding energy is 4.41 kcal/mol, which supports Gotch and Zwier's experimental results[5] and the review of Mons *et al*.[31]

3.2. H_2O-C_6H_6

Table 2 presents the DFT and ab initio calculations for the H_2O-C_6H_6 complex. In the table, we used the zero-point vibrational energy of Feller[37] and the experimental[24,27] ground state dissociation energy D_0 to obtain the accurate equilibrium dissociation energy D_e. From D_e-cp in Table 1, we can see that PW91, MPW1B95, MPWB1K, PW6B95, and PWB6K perform much better than B3LYP for calculating the dissociation energy and geometry of the benzene-water OH···π hydrogen bonded complex. B3LYP seriously underestimates the interaction energy and overestimates the intermolecular distance. The performance of MPW1B95, MPWB1K and PW6B95 is comparable to the CCSD(T)/aVDZ calculations. The best DFT method for energetics (with the counterpoise correction) is the PWB6K method with the DIDZ basis; it gives better performance than MP2/aVTZ. The best DFT method for geometries is PW6B95/DIDZ, and PW91 seriously overestimates the intermolecular distance for the H_2O-C_6H_6 complex.

If we look at the D_e column without counterpoise correction, we can see that MP2 and CCSD(T) overestimate the binding energy and that DFT gives much better performance. Table 1 shows that the BSSE corrections for DFT methods are much smaller than those for the MP2 or CCSD(T) calculations.

3.3. NH_3-C_6H_6 and HCl-C_6H_6

Table 3 gives the DFT results for the NH_3-C_6H_6 and HCl-C_6H_6 complexes. The trends in Table 3 is similar to that in Table 2. B3LYP seriously underestimates the strength of these π hydrogen bonded complexes. The D_e-cp columns in Table 3 show that MP2/MG3S gives the best energetics, and PW91, MPW1B95, MPWB1K, PW6B95, and PWB6K perform much better than B3LYP for calculating the dissociation energies. However, PW91, like B3LYP, seriously overestimates the intermolecular distances for the NH_3-C_6H_6 complex.

The experiments indicate that D_e is 2.0 kcal/mol large for HCl than NH_3, with H_2O intermediate. PWB6K predicts an increase of 1.4-2.0 kcal/mol, also with H_2O intermediate. PW91 predicts an increase of 1.1-1.6 kcal/mol, and B3LYP predicts an increase of 0.8-2.2 kcal/mol.

3.4. H_2O-indole and H_2O-methylindole

Table 4 gives the results for the indole-water and methylindole-water systems. For the indole-water system, there are two different types of hydrogen bonds; one is the conventional nearly linear NH···O hydrogen bond, and the other one is the π facial hydrogen bond. Note that B3LYP erroneously gives two π bonded structures; in these structures the water is bonded to either the pyrrole or the phenyl ring. Our calculations show that PW91 also erroneously gives two π bonded minima. The other four DFT methods and MP2 give only one minimum-energy OH···π bonded structure. The binding energy for B3LYP and PW91 shown in Table 4 is the binding energy of the most stable OH···π bonded complex. van Mourik commented that "DFT's inability to account for dispersion causes the water to move away from the center of the π-electron cloud. This effect explains the partition of the single π-bonded indole-water minimum into two distinct DFT minima, each having the water on opposite sides of the aromatic system." [43] This is a reasonable explanation, provided one keeps in mind that these system are not in the zero-overlap dispersion regime.

In a recent paper,[55] we have shown that MPW1B95, MPWB1K, PW6B95, and PWB6K give much better performance than B3LYP for interactions dominated by dispersion-like interactions. This is consistent with these four new methods giving correct geometries even with the DIDZ basis set, but again we emphasize that the energy of binding is not zero-overlap dispersion energy in the present cases. At a minimum-energy geometry, the total gradient is zero; therefore, if one can separate repulsive interactions from attractive ones, their gradients would be equal in magnitude. Thus, even if the attractive part of the interaction were entirely due to dispersion (which is not the case

even for the interaction of rare gas atoms), dispersion would account for at most half of the gradient, and usually one must also consider electrostatics, polarization, charge transfer, change in interatomic correlation, and so forth. The dispersion interactions occur in the second order of the Rayleigh-Schrödinger perturbation theory (RSPT). At the equilibrium geometry of He_2, the exchange energy and the first-order RSPT term are respectively equal to −55% and +8% of the second-order RSPT term.[67] In light of these considerations, it is interesting to see how well various functionals can represent the net interaction energy.

First we consider the results for the conventional hydrogen bonding complex, which is the global minimum for the indole-water system. If one considers the counterpoise-corrected dissociation energy obtained in the calculation with the larger basis and compares to the average of the two experimental results counterpoise-corrected dissociation energy, B3LYP underestimates the binding energy of the conventional hydrogen bonding structure by only 1.5 kcal/mol, and PW91, MPW1B95, MPWB1K, PW6B95, and PWB6K give only slightly better results (underestimation of 0.6 – 1.2 kcal/mol).

Next consider the π acceptor cases. There is no experimental result for the indole-water OH···π hydrogen bonded complex because it is not the global minimum. We therefore use van Mourik's estimated MP2 complete basis set results, with a small (0.14 kcal/mol) correction for possible changes at the CCSD(T) level, as the reference. Although this is not as reliable as experiment, it is probably accurate enough to test DFT for this case. From Table 4, we can see that, for the counterpoise corrected DFT calculations, PWB6K/DIDZ gives the best binding energy, and this is also confirmed by the results for the methylindole-water complex, where an experimental result is available. For both O-H···π hydrogen bonded complexes, MPW1B95, MPWB1K, PW6B95, and PWB6K show much better performance than the B3LYP method. Although PW91 gives strong interaction for the normal hydrogen bonding (indole-H_2O-NH), it is inferior to

PW6B95, MPWB1K, and PWB6K for the π hydrogen bonding, and it overestimates the intermolecular distances for the π hydrogen bonded complexes (as compared to the MP2/aVTZ geometries). Furthermore, tor both OH···π hydrogen bonded complexes, B3LYP seriously underestimates the binding energy and overestimates the intermolecular distance; this is consistent with the results in Tables 2 and 3.

Table 5 summarizes the error average over the six complexes. All four of the new methods considered here do better than MP2, on the average, whereas B3LYP is 1.8 times worse. Table 5 shows that independent of which basis set we consider and independent of whether or not we correct for BSSE, the three most reliable DFT methods in Table 5 are PWB6K, MPWB1K, and PW6B95. In three of the four comparisons all three methods perform better than MP2, and in all four cases, PWB6K performs better. However, the key issue is not really whether DFT does better than MP2, but rather that, since MP2 is universally acknowledged to provide a reasonable physical model for this kind of interaction, DFT with the new functionals has comparable accuracy. Since DFT is much more affordable than MP2 for all but the smallest systems, since it is less sensitive to BSSE, and since these new functionals have previously been shown to provide useful accuracy for a variety of other physical quantities, [54-56] this opens up new possibilities for realistic modeling of molecular recognition, host-guest chemistry, protein folding, crystal packing, and many other condensed-phase chemical, physical and biological phenomena.

4. Concluding remarks

Although DFT does not predict true dispersion interactions in the weak interaction region of zero overlap, it can still be useful for predicting correlation energy and even dispersion-like interactions in the region of overlap near the equilibrium geometry of even noncovalent complexes if one has an accurate enough functional. In the present study, we showed that four newly developed DFT methods are all capable of qualitatively and even semiquantitatively describing the π hydrogen-bonded complexes,

for which the popular B3LYP method fails. Our calculations show that the PWB6K density functional gives especially accurate energetics and geometrical prediction for the π hydrogen bonding interactions. We recommend this method for investigating large hydrogen bonded systems in which the face of a π system is the hydrogen bond acceptor as well as for other noncovalent interactions of overlapping system in which dispersion-like interactions play a role.

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Table 1. Benchmark results (in kcal/mol) for the binding energies of the H_2O-C_6H_6, NH_3-C_6H_6, and HCl-C_6H_6 complexes [a]

Complexes	HF/IB	ΔMP2/IB [b]	MP2/IB	Δ(CCSD(T)-MP2)	CCSD(T)/CBS [c]	Exp.
H_2O-C_6H_6	0.18	3.48	3.66	-0.29	3.37	3.44 ± 0.09, [d] 3.25 ± 0.28 [d]
NH_3-C_6H_6	-0.82	3.56	2.73	-0.29	2.44	2.45 ± 0.12 [14]
HCl-C_6H_6	-0.35	5.46	5.11	-0.70	4.41	5.82, [e] 2.83≤D_e≤4.83 [e]

[a] MP2/MG3S geometries are used for the calculations in this table, and see text for description of the MG3S basis set. All calculated energies are BSSE corrected.
[b] The extrapolated (ΔE_{MP2}-ΔE_{HF}) results.
[c] This column gives D_e estimated using Eq. (1).
[d] Experimental D_0 [24,27]+ theoretical ZPE. [37]
[e] Experimental D_0 [3,5] + theoretical ZPE. [36]

Table 2. Binding energies (in kcal/mol) and intermolecular distance[a] (in angstroms) for the H_2O-C_6H_6 complex

Method	Ref.	R_e	D_e	D_e-cp
MPW1B95/DIDZ	This work	3.27	3.05	2.55
MPW1B95/MG3S	This work	3.24	2.85	2.40
MPWB1K/DIDZ	This work	3.23	3.21	2.70
MPWB1K/MG3S	This work	3.22	3.04	2.57
PW6B95/DIDZ	This work	3.28	3.24	2.74
PW6B95/MG3S	This work	3.26	3.03	2.59
PWB6K/DIDZ	This work	3.21	3.72	3.22
PWB6K/MG3S	This work	3.21	3.54	3.10
PW91/DIDZ	This work	3.53	3.21	2.70
PW91/MG3S	This work	3.49	2.91	2.44
B3LYP/DIDZ	This work	3.71	1.98	1.55
B3LYP/MG3S	This work	3.68	1.78	1.35
MP2/DIDZ	This work	3.28	4.08	2.16
MP2/MG3S	This work	3.21	4.12	2.96
MP2/DZP	35		4.37	1.76
MP2/aVDZ	37	3.24	4.84	2.89
CCSD(T)/aVDZ	37	3.24	4.56	2.68
MP2/aVTZ	37	3.21	4.01	3.13
CCSD(T)/aVTZ	37		3.85	
MP2/VQZ	37	3.21	4.06	3.42
MP2/V5Z	37		3.75	3.42
Est. MP2 CBS	37		3.9 ± 0.2	
Expt.	8	3.32 [b]		
Expt.	7	3.35 [b]		
Expt.	23	3.33 [b]		
Expt.	24		3.25 [c]	3.25 [c]
Expt.	27		3.40 [c]	3.40 [c]

[a] The intermolecular distance is defined as the distance between the center of mass of water and the center of mass of benzene in the complex. In this table, aVDZ means aug-cc-pVDZ, and aVTZ means aug-cc-pVTZ.
[b] These are experimental values for r_0.
[c] We used the the zero-point vibrational energy of Feller[37] and experimental D_0[24,27] to obtain the experimental equilibrium dissociation energy D_e

Table 3. Binding energies (in kcal/mol) and intermolecular distance[a] (in angstroms) for the NH_3-C_6H_6 and HCl-C_6H_6 complexes

Method	NH_3-C_6H_6			HCl-C_6H_6		
	R_e	D_e	D_e-*cp*	R_e	D_e	D_e-*cp*
MPW1B95/DIDZ	3.67	1.66	1.38	3.63	3.58	3.08
MPW1B95/MG3S	3.61	1.57	1.34	3.63	3.03	2.68
MPWB1K/DIDZ	3.56	1.79	1.49	3.61	3.82	3.31
MPWB1K/MG3S	3.58	1.72	1.46	3.59	3.26	2.91
PW6B95/DIDZ	3.67	1.86	1.58	3.65	3.66	3.18
PW6B95/MG3S	3.62	1.76	1.53	3.67	3.14	2.82
PWB6K/DIDZ	3.55	2.27	1.97	3.61	4.25	3.75
PWB6K/MG3S	3.55	2.19	1.94	3.59	3.72	3.34
PW91/DIDZ	4.01	1.88	1.55	3.67	3.47	2.95
PW91/MG3S	3.82	1.64	1.42	3.70	2.89	2.51
B3LYP/DIDZ	4.33	0.95	0.69	3.81	2.13	1.70
B3LYP/MG3S	4.22	0.71	0.58	3.86	1.68	1.41
MP2/DIDZ	3.48	3.08	1.24	3.52	5.26	2.51
MP2/MG3S	3.43	3.05	2.17	3.45	5.71	4.05
MP2/aug-cc-pVDZ [b]		4.19	2.17		4.63	4.06
MP2/aug-cc-pVTZ [b]		3.31	2.49		6.39	5.72
CCSD(T)/CBS			2.44			4.41
Expt.	3.59 [c]		2.45 [d]			2.8-5.8 [e]

[a] The distance between the center of mass of the interacting molecules.
[b] Evaluated at the MP2/MG3S geometries.
[c] Ref. [9]
[d] Ref. [14]
[e] See discussion in Section 3.1.

Table 4. Binding energies (in kcal/mol) and intermolecular distance[a] (in angstroms) for the indole-water and methylindole-water complexes

Method	Ref.	indole-H_2O-NH			indole-H_2O-πA			methylindole-H_2O		
		R_e	D_e	D_e-cp	R_e	D_e	D_e-cp	R_e	D_e	D_e-cp
MPW1B95/DIDZ	This work	1.98	6.27	5.38	3.19	4.61	3.63	3.11	5.31	4.35
MPW1B95/MG3S	This work	2.02	5.16	4.75	3.19	4.04	3.47	3.09	4.64	4.02
MPWB1K/DIDZ	This work	1.97	6.40	5.53	3.17	4.82	3.99	3.08	5.55	4.61
MPWB1K/MG3S	This work	2.01	5.28	4.88	3.16	4.27	3.70	3.07	4.91	4.29
PW6B95/DIDZ	This work	1.99	6.37	5.46	3.21	4.78	3.81	3.12	5.48	4.53
PW6B95/MG3S	This work	2.03	5.28	4.88	3.21	4.19	3.65	3.11	4.81	4.21
PWB6K/DIDZ	This work	1.97	6.86	5.98	3.16	5.38	4.28	3.06	6.17	5.22
PWB6K/MG3S	This work	2.00	5.86	5.47	3.15	4.59	4.05	3.06	5.56	4.94
PW91/DIDZ	This work	1.93	7.07	5.96	3.30	4.69	3.85	3.21	5.14	4.11
PW91/MG3S	This work	1.96	5.97	5.43	3.30	4.19	3.60	3.25	4.54	3.89
B3LYP/DIDZ	This work	1.98	5.99	5.04	3.39	3.31	2.68	3.33	3.63	2.86
B3LYP/MG3S	This work	2.01	4.94	4.54	3.39	2.83	2.42	3.36	3.10	2.63
MP2/DIDZ	This work	1.95	7.66	5.49	3.18	6.30	3.57	3.08	7.53	4.33
MP2/MG3S	This work	1.95	6.48	5.37	3.14	5.87	4.35	3.02	6.77	5.08
MP2/DZP*i*	[39]	1.85	8.34	5.38	3.05	7.96	3.83		9.07	4.45
MP2/aVDZ	[39]	1.95	6.72	5.38	3.10	6.63	4.22		7.64	5.03
MP2/aVTZ	[39]	1.95	6.36	5.64	3.13	5.78	4.73			
Est. MP2 CBS	[39]			5.76			4.87			

Extrap.	This work	5.94 [b]	5.15 [b]	
Average	This work	5.85 [c]	5.01 [c]	
Expt.	[29]	6.15 [d]		5.72 [d]
Expt.	[25]	5.98 [d]		

[a] The intermolecular distance is defined as the O···H distance in the O···H-N hydrogen bond for the indole-H_2O-NH complex. The intermolecular distance is defined as the distance between the oxygen of the water and the indole plane for the indole-H_2O-π and methylindole-H_2O complexes. In this table, aVDZ denotes aug-cc-pVDZ, and aVTZ denotes aug-cc-pVTZ.

[b] D_e(extrap.)= D_e[CCSD(T)/DZP*i*] – D_e[MP2/)/DZP*i*] +Est. MP2 CBS, where the three components are from Ref. 39

[c] Average of two previous rows.

[b] We used the scaled (scale factor is 0.9721)[54] harmonic zero-point vibrational energies calculated by the MPW1B95 method and the experimental D_0 to obtain the experimental equilibrium dissociation energy D_e.

Table 5. Mean unsigned errors in binding energies (kcal/mol) [a]

Method	DIDZ [b]		MG3S [b]		average
	nocp	cp	nocp	cp	
MPW1B95	0.48	1.10	0.95	1.39	0.98
MPWB1K	0.34	0.89	0.75	1.19	0.80
PW6B95	0.37	0.95	0.79	1.21	0.83
PWB6K	0.39	0.43	0.33	0.69	0.46
PW91	0.59	0.98	0.81	1.28	0.91
B3LYP	1.46	2.04	1.96	2.28	1.94
MP2	1.27	1.25	0.96	0.71	1.05

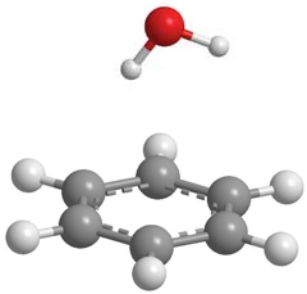
[a] The accurate value from which deviations are computed is taken as the experimental value or average experimental values for H_2O-C_6H_6 (3.325), NH_3-C_6H_6 (2.45), indole-H_2O-NH (6.065), and methylindole (5.72), estimated CCSD(T) CBS value for HCl-C_6H_6 (4.41), and estimated MP2 CBS value for indole-H_2O-πA (4.87).
[b] DIDZ denotes the 6-31+G(d,p) basis set, and see text for the MG3S basis set.
[c] Aaverage over previous four columns.

Figure caption

Figure 1. Structures of the complexes studied. (A) H_2O-C_6H_6, π facial acceptor (B) NH_3-C_6H_6 Benzene-water, π facial acceptor. (C) HCl-C_6H_6, π facial acceptor. (D) Indole-water: normal hydrogen donor structure, denoted NH. (E) Indole-water: π facial acceptor, denoted πA. (F) Methylindole-water: π facial acceptor.

Figure 1

(A)



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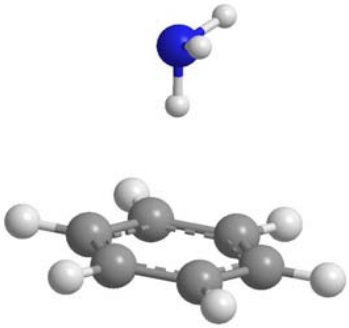

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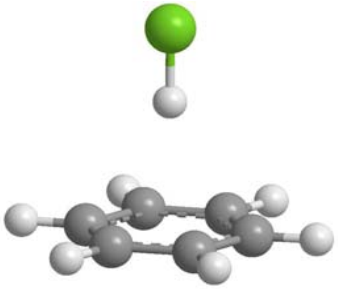

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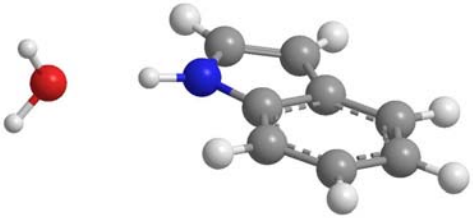

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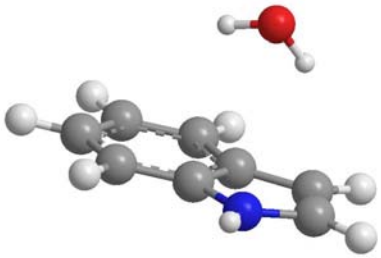

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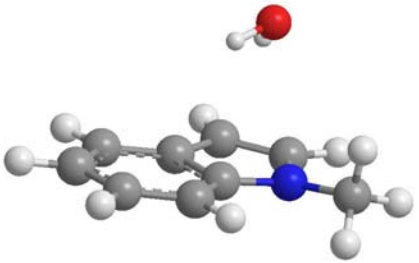

Table of Content (Graphical)