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Benchmark Data for Noncovalent Interactions in HCOOH...Benzene Complexes and Their Use for Validation of Density Functionals

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Abstract: We present benchmark energetic data for the HCOOH...benzene complexes. The benchmark data were determined by a composite approach based on CCSD(T) calculations. Final binding energies (kcal/mol) are in the range of 1.6–4.8 kcal/mol, and they were used as reference data to test density functionals in the literature. Among the tested local density functionals without empirical dispersion corrections, M06-L is the best performing functional, and M06-L/6-31+G(d,p) gives a mean unsigned error (MUE) of only 0.15 kcal/mol. PBEsol and SOGGA also show promising performance. The best local DFT-D methods are BLYP-D and PBEsol-D, and they give an MUE of 0.15 kcal/mol after removing basis set superposition errors by the counterpoise approach. Empirical dispersion corrections greatly improve the descriptions of noncovalent interactions in HCOOH...benzene dimers. The calculated benchmark data and intermolecular potential are useful for the parametrizations of new force fields and coarse-grained models for chemical species such as the acrylic polymers.

1. Introduction

An understanding of noncovalent interactions between a polar molecule and an aromatic system is of fundamental interest since these interactions are common not only in biological systems^{1,2} but also in many areas of chemistry and materials science.^{3–7} An important example of this type of interaction, water...benzene dimer, has been extensively studied both experimentally and theoretically.^{8–14} Recently Crittenden¹⁵ carried out a systematical and theoretical study of the long-range noncovalent interactions between benzene and a series of hydrides and rare gas atoms. More recently, Imai et al.¹⁶ reported a computational study of the amide- π interactions between formamide (HCONH₂) and benzene, and Ottiger et al.¹⁷ performed a theoretical study of the amide-benzene interactions in the 2-pyridone...benzene complexes. In the present study, we focus on understanding the noncovalent interactions between formic acid (HCOOH) and benzene.

The HCOOH...benzene complex can be considered as a model system for understanding the side-chain interactions in acrylic polymers (or resins), because they are commonly being

used in the coating and printing industry. Furthermore, the HCOOH...benzene dimer can be viewed as a model system for studying pigment-polymer interactions since common pigments such as those based on Cu-phthalocyanine have benzene rings in their structures, and acrylic polymers have –COOH side-chains. It is important to understand such physical interactions for rational design of future high-performance materials for next-generation printing materials and technology.

The experimental or computational studies of the HCOOH...benzene complex are scarce in the literature. An objective of the present study is to use Møller–Plesset second order perturbation theory (MP2)¹⁸ and coupled cluster theory^{19,20} with single and double excitations and a quasiperturbative treatment of connected triple excitations (CCSD(T)) to characterize the HCOOH...benzene complexes and to develop benchmark energetic data for interaction energies in HCOOH...benzene dimers. A further goal of our study is to validate a number of low-cost density functional theory (DFT) methods and to determine if these can describe the energetics of noncovalent interactions in HCOOH...benzene complexes.

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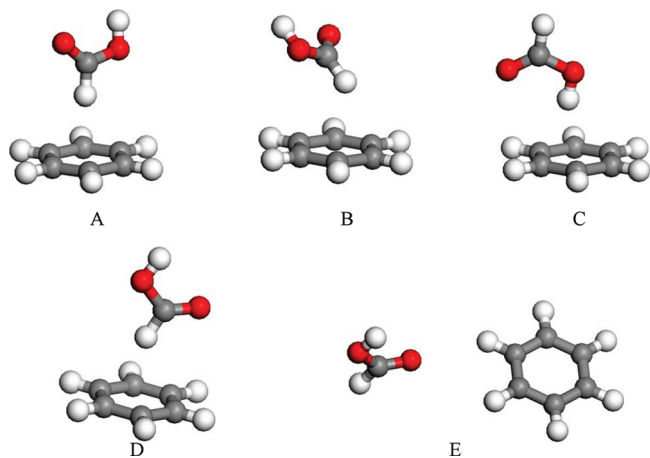


Figure 1. Five stationary points on the potential energy surface of an HCOOH...benzene complex.

2. Computational Methods

We have employed MP2¹⁸ and the 6-311+G(2df,2p) basis set²¹ to optimize the geometries of the HCOOH...benzene complexes without any geometrical constraints. We started with many initial guesses of the dimer configurations for optimizations, following the procedure described in a previous paper for HCONH₂...benzene.¹⁶ Five stationary points have been located as the minimum structures on the MP2/6-311+G(2df,2p) potential energy surface, and they are shown in Figure 1.

We estimated the CCSD(T) complete basis limit binding energies in these five complexes as follows

$$D_e(\text{CCSD(T)}/\text{CBS}) = D_e(\text{MP2}/\text{CBS}) + D_e(\text{CCSD(T)}/\text{SB}) - D_e(\text{MP2}/\text{SB}) \quad (1)$$

where CBS denotes the complete-basis limit, and SB denotes a small basis (aug-cc-pVDZ). The MP2/CBS energies are extrapolated by

$$E^{\text{MP2}}(n) = E_{\infty}^{\text{MP2}} + An^{-3} \quad (2)$$

where n represents the highest angular momentum in an augmented correlation-consistent basis set, $n = 3$ for the aug-cc-pVTZ basis, and $n = 4$ for the aug-cc-pVQZ basis sets. We also examine a lower-cost MP2/IB extrapolation using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. IB denotes the separate extrapolation^{22–24} of Hartree–Fock and MP2 correlation energies to the infinite-basis (IB) limit. The Hartree–Fock energies are extrapolated by

$$E^{\text{HF}}(n) = E_{\infty}^{\text{HF}} + A^{\text{HF}}n^{-\alpha} \quad (3)$$

and the MP2 correlation energies are extrapolated by

$$E^{\text{cor}}(n) = E_{\infty}^{\text{cor}} + A^{\text{cor}}n^{-\beta} \quad (4)$$

The parameters α and β in eqs 3 and 4 are determined in a previous paper;²⁴ the value used for α is 4.93, and that for β is 2.13. Combining MP2/IB with the (CCSD(T)–MP2) correction evaluated at the aug-cc-pVDZ basis set, one can define an estimated CCSD(T)/IB binding energies

$$D_e(\text{CCSD(T)}/\text{IB}) = D_e(\text{MP2}/\text{IB}) + D_e(\text{CCSD(T)}/\text{SB}) - D_e(\text{MP2}/\text{SB}) \quad (5)$$

This composite approach defined in eq 5 has been shown²³ to give very good agreement with experiments for the predictions of binding energies in the H₂O...benzene and NH₃...benzene systems, provided that counterpoise (Cp) corrections for basis set superposition error (BSSE) are included. Therefore we performed all benchmark calculations with Cp corrections^{25–27} for BSSE.

We have tested density functionals with the MP2/6-311+G(2df,2p) geometries. The tested functionals can be classified according to various rungs of “Jacob’s ladder”.²⁸ The lowest rung is the local spin density approximation (LSDA), in which the density functional depends only on spin densities, and the second rung is the generalized gradient approximation (GGA, in which the density functional depends on spin densities and their reduced gradient). The third-rung functionals, meta-GGAs, also depends on the spin kinetic energy densities. The fourth rung is hyper GGA,²⁸ which employs full or partial exact Hartree–Fock (HF) exchange. There are two types of hyper GGAs on the fourth rung, namely the hybrid GGAs (HF + GGA) and hybrid meta-GGAs (HF + meta-GGA). In this work, the tested conventional functionals include one LSDA,^{29–31} 9 GGAs (BLYP,^{32,33} BP86,^{32,34} G96LYP,^{33,35} HCTH,³⁶ mPWPW,³⁷ OLYP,^{33,38} PBE,³⁹ PBEsol,⁴⁰ and SOGGA⁴¹), three meta-GGAs (M06-L,⁴² TPSS,^{43,44} and VSXC⁴⁵), 12 hybrid GGAs (B3LYP,⁴⁶ B97-1,³⁶ B97-2,⁴⁷ B98,⁴⁸ BHandH,⁴⁹ BHandH-LYP,⁴⁹ MPW1K,⁵⁰ mPW1PW,³⁷ MPW3LYP,^{33,37,51} O3LYP,^{38,52} PBE0,³⁹ X3LYP⁵³), and 9 hybrid meta-GGAs (BMK,⁵⁴ PW6B95,⁵⁵ PWB6K,⁵⁵ M05,⁵⁶ M05-2X,⁵⁷ M06,⁵⁸ M06-2X,⁵⁸ M06-HF,⁵⁹ and TPSSH^{43,44}).

Recently several DFT-D schemes have been developed^{60–63} by augmenting the conventional DFT energy with a damped empirical dispersion term ($-C_6R^{-6}$), these DFT-D schemes have been shown to give much improved performance for noncovalent interactions. In the present study, we test B97-D,⁶⁰ TPSS-D,⁶⁰ BP86-D,⁶⁰ B3LYP-D,⁶⁰ PBE-D,⁶⁰ PBEsol-D,⁶¹ ω B97X-D,⁶² PBE0-D,⁶³ BMK-D,⁶³ M06-L-D,⁶³ M06-D,⁶³ and SOGGA-D. SOGGA-D is defined in the present study by using the same empirical dispersion corrections as PBEsol-D.

In the Grimme’s dispersion damping function⁶⁰ for DFT-D calculations, the van der Waals radii are derived from the radius of the 0.01 a_0^{-3} electron density contour from ROHF/TZV calculations of the atoms in the ground state, and Grimme used a scale factor of 1.1 to scale these radii. The van der Waals radii in Table 1 of ref 60 are scaled values. In PBEsol-D (also in SOGGA-D), the scale factor is increased to 1.42.⁶¹ We implemented the new scale factor in the locally modified Gaussian09 program for PBEsol-D and SOGGA-D calculations.

All DFT calculations have been performed with the locally modified GAMESS,⁶⁴ NWChem,⁶⁵ and Gaussian09⁶⁶ programs.

3. Results and Discussion

3.1. Stationary Points on the Potential Energy of HCOOH...Benzene Noncovalent Complexes. Figure 1 shows the five minimum structures located by the MP2/6-

Table 1. Benchmark Results (in kcal/mol) for the Binding Energies^a of the HCOOH...Benzene Complexes

complex	HF/IB ^b	ΔMP2/IB ^c	MP2/IB ^d	MP2/CBS ^e	Δ(CCSD(T)-MP2) ^f	CCSD(T)/IB ^g	CCSD(T)/CBS ^h
A	-0.63	4.40	3.77	3.60	-0.45	3.32	3.15
B	-1.20	5.25	4.05	3.88	-0.58	3.48	3.30
C	0.18	5.51	5.69	5.44	-0.65	5.04	4.79
D	-0.82	4.69	3.87	3.70	-0.47	3.41	3.23
E	0.19	1.54	1.73	1.68	-0.06	1.67	1.62

^a The binding energy D_e is defined in the present study as the equilibrium dissociation energy of the complexes dissociated into HCOOH and benzene. All calculations employed MP2/6-311+G(2df,2p) geometries. ^b Extrapolated ΔE_{HF} with eq 3 and the aug-cc-pVDZ and aug-cc-pVTZ basis sets. ^c The extrapolated ($\Delta E_{\text{MP2}} - \Delta E_{\text{HF}}$) results with eq 4 and the aug-cc-pVDZ and aug-cc-pVTZ basis sets. ^d The sum of HF/IB and $\Delta\text{MP2/IB}$. ^e The extrapolated ΔE_{MP2} results with eq 2 and the aug-cc-pVTZ and aug-cc-pVQZ basis sets. ^f This term is evaluated with the aug-cc-pVDZ basis set. ^g This column gives D_e estimated using eq 5, i.e. the summation of values in the MP2/IB and $\Delta(\text{CCSD(T)} - \text{MP2})$ columns. ^h This column gives D_e estimated using eq 1, i.e. the summation of values in the MP2/CBS and $\Delta(\text{CCSD(T)} - \text{MP2})$ columns.

Table 2. Binding Energies and Mean Errors (in kcal/mol) for Local Density Functionals^a

method	A	B	C	D	E	MSE ^b	MUE ^c
best estimate ^d	3.15	3.30	4.79	3.23	1.62		
M06-L	2.60	2.98	4.60	2.71	1.19	-0.40	0.40
SOGGA	2.47	2.38	4.56	2.53	1.29	-0.57	0.57
PBESol	2.29	2.20	4.30	2.35	1.18	-0.76	0.76
LSDA	4.52	4.81	7.12	4.76	2.48	1.52	1.52
PBE	1.27	1.02	2.85	1.25	0.91	-1.76	1.76
TPSS	0.71	0.30	2.07	0.61	0.48	-2.39	2.39
mPWPW	0.42	0.01	1.80	0.31	0.32	-2.65	2.65
τ -HCTH	0.07	-0.50	1.15	-0.14	0.45	-3.01	3.01
HCTH	-0.10	-0.63	0.96	-0.27	0.92	-3.04	3.04
BP86	-0.05	-0.45	1.32	-0.13	-0.16	-3.11	3.11
BLYP	-0.73	-1.25	0.29	-0.85	-0.02	-3.73	3.73
OLYP	-2.45	-3.38	-1.72	-2.77	-0.66	-5.41	5.41
G96LYP	-2.87	-3.67	-2.03	-3.08	-1.76	-5.90	5.90
VSXC	9.14	11.65	12.71	10.72	4.21	6.47	6.47

^a Tested with the 6-311+G(2df,2p) basis set and MP2/6-311+G(2df,2p) geometries. ^b MSE denotes mean signed error (same as mean deviation, MD). ^c MUE denotes mean unsigned error (same as mean absolute deviation, MAD). ^d Taken from the CCSD(T)/CBS results of Table 1.

311+G(2df,2p) level of theory. The first four complexes (A–D) are π -hydrogen bonded complexes, in which the hydrogen bond acceptor is the π -cloud on the benzene molecule. The fifth complex (E) is bound by the interaction between the sp^2 oxygen in HCOOH and two hydrogens of benzene.

3.2. Benchmark Calculations. Table 1 gives the benchmark results for the noncovalent interaction energies in the five HCOOH...benzene complexes.

Table 1 shows that Hartree–Fock (the HF/IB column of Table 1) theory severely underestimates the noncovalent interactions in the HCOOH...benzene complexes because HF theory gives small or repulsive (or negative) binding energies (at the MP2/6-311+G(2df,2p) geometries). The attractive interactions in these complexes are mostly due to medium-range correlation energies, which are absent in Hartree–Fock theory.

As shown in Table 1, the MP2/IB calculations agree with MP2/CBS within 0.2 kcal/mol, but MP2/IB is a much less expensive method than MP2/CBS. For large systems, MP2/IB is an efficient alternative to the MP2/CBS approach.

Table 3. Binding Energies and Mean Errors (in kcal/mol) for Hybrid Density Functionals^a

method	A	B	C	D	E	MSE ^b	MUE ^c
best estimate ^d	3.15	3.30	4.79	3.23	1.62		
PWB6K	2.89	2.97	4.63	3.09	1.62	-0.18	0.18
M05-2X	3.32	3.59	5.43	3.43	1.61	0.26	0.26
M06	2.54	2.90	4.49	2.63	1.26	-0.45	0.45
M06-2X	3.54	4.04	5.68	3.77	1.59	0.50	0.52
PW6B95	2.17	2.18	3.78	2.35	1.22	-0.88	0.88
M05	1.81	1.79	3.39	1.93	1.56	-1.12	1.12
M06-HF	4.44	4.92	6.60	4.59	1.77	1.24	1.24
PBE0	1.58	1.34	3.20	1.55	0.98	-1.49	1.49
B97-1	1.55	1.34	3.00	1.54	1.15	-1.50	1.50
BHandH	4.66	4.94	7.01	4.89	2.72	1.63	1.63
MPW1K	1.36	1.07	2.89	1.29	0.74	-1.75	1.75
B98	1.20	0.91	2.57	1.14	0.94	-1.87	1.87
BMK	1.09	1.08	2.78	1.31	0.25	-1.92	1.92
MPW3LYP	1.10	0.80	2.42	1.05	1.13	-1.92	1.92
BHandHLYP	1.08	0.77	2.41	1.03	0.98	-1.97	1.97
τ -HCTHh	1.04	0.77	2.51	0.98	0.64	-2.03	2.03
mPW1PW	0.95	0.60	2.42	0.86	0.56	-2.14	2.14
TPSSH	0.87	0.48	2.27	0.78	0.54	-2.23	2.23
TPSS1KCIS	0.81	0.42	2.11	0.72	0.66	-2.28	2.28
X3LYP	0.74	0.40	2.04	0.68	0.83	-2.28	2.28
B97-2	0.27	-0.16	1.53	0.14	0.31	-2.80	2.80
B3LYP	0.20	-0.21	1.42	0.12	0.46	-2.82	2.82
O3LYP	-1.59	-2.38	-0.67	-1.85	-0.27	-4.57	4.57

^a Tested with the 6-311+G(2df,2p) basis set and MP2/6-311+G(2df,2p) geometries. ^b MSE denotes mean signed error (same as mean deviation). ^c MUE denotes mean unsigned error (same as mean absolute deviation, MAD). ^d Taken from the CCSD(T)/CBS results of Table 1.

Table 4. Binding Energies and Mean Errors (in kcal/mol) for DFT-D^a

method	A	B	C	D	E	MSE ^b	MUE ^c
best estimate ^d	3.15	3.30	4.79	3.23	1.62		
M06-D	3.25	3.71	5.31	3.37	1.50	0.21	0.26
BLYP-D	3.52	3.58	5.22	3.61	1.38	0.24	0.34
M06-L-D	3.31	3.79	5.42	3.46	1.42	0.26	0.34
ω B97X-D	3.63	3.80	5.14	3.63	1.39	0.30	0.39
BMK-D	3.39	3.70	5.46	3.73	1.01	0.24	0.48
PBEsol-D	3.68	3.72	5.77	3.69	1.68	0.49	0.49
BP86-D	3.67	3.77	5.63	3.78	1.06	0.36	0.59
B3LYP-D	3.92	4.02	5.73	4.02	1.68	0.66	0.66
SOGGA-D	3.86	3.90	6.03	3.88	1.79	0.67	0.67
PBE-D	3.93	4.04	5.94	4.04	1.79	0.73	0.73
PBE0-D	4.06	4.16	6.08	4.16	1.79	0.83	0.83
TPSS-D	4.25	4.33	6.19	4.33	1.64	0.93	0.93

^a Tested with the 6-311+G(2df,2p) basis set and MP2/6-311+G(2df,2p) geometries. ^b MSE denotes mean signed error (same as mean deviation). ^c MUE denotes mean unsigned error (same as mean absolute deviation, MAD). ^d Taken from the CCSD(T)/CBS results of Table 1.

From Table 1, we can see that the small-basis CCSD(T) corrections contribute -0.06 to -0.65 kcal/mol to the final dissociation energies. Among the four π -hydrogen bonded complexes, complex C has the largest binding energy; the hydrogen donor in complex C is the $-\text{OH}$ group of formic acid, which is a stronger hydrogen bond donor than the $\text{C}-\text{H}$ hydrogen donor in the other three π -hydrogen bonded complexes (A, B, and D). Complex E is the weakest HCOOH...benzene dimer.

The largest binding energy in HCOOH...benzene dimers is 4.79 kcal/mol (complex C), which is about 0.2 kcal/mol less than the binding energy in water dimer (5.02 kcal/mol).⁶⁷ The binding strength in complex C is stronger than those between benzene and first- and second-row hydrides (among them $\text{HF}\cdots\text{benzene}$ has the largest binding energy of 4.3 kcal/mol, and $\text{H}_2\text{O}\cdots\text{benzene}$ has a binding energy of 3.2 kcal/mol).¹⁵ According to Imai et al. report,¹⁶ the largest binding energy in $\text{HCONH}_2\cdots\text{benzene}$ is 3.0 kcal/mol, which is about 1.8 kcal/mol smaller than the binding energy in complex C; this result agrees with the fact that HCOOH is a much stronger hydrogen bond donor than HCONH_2 .

3.3. Performance of Local Density Functionals. Table 2 gives the test results for local density functionals; we use the word “local” in the analogy as Becke,⁶⁸ so that it includes spin density gradient and spin kinetic energy density (as well as local spin density) but excludes Hartree–Fock exchange.

Among the tested local functionals, only LSDA and VSXC overestimate the binding energies, as shown by their positive MSEs. Other functionals underestimate the binding energies. Most of the tested local density functionals give a bad performance with the major exception being the M06-L, SOGGA, and PBEsol functionals, which gives a mean unsigned error (MUE) of 0.40, 0.57, and 0.76 kcal/mol, respectively. Other local functionals have MUEs greater than 1 kcal/mol. It is not surprising that M06-L give a good performance for noncovalent interactions in HCOOH...benzene complexes, since the training set of the M06-L functional contains some noncovalent interaction data. The surprisingly good performance of the nonempirical SOGGA and PBEsol functionals is likely due to their diminished gradient dependence⁴¹ as compared to PBE. As shown in Table 2, LSDA overestimate the binding strength, whereas PBE underestimates them. In PBE, the second-order gradient expansion for exchange is not respected, whereas in SOGGA and PBEsol, the gradient expansion for exchange has been restored,^{40,41} and their exchange enhancement factors are between LSDA and PBE, so both SOGGA and PBEsol perform better than PBE. At the high reduced gradient region, which is important for noncovalent interactions, SOGGA diminishes more gradient correction than PBEsol,⁴¹ so SOGGA gives slightly stronger binding than PBEsol. Recent studies^{40,41,69,70} showed that PBEsol and SOGGA give a very much better performance for lattice constant predictions than PBE and LSDA, but M06-L is less accurate for lattice constants than PBEsol and SOGGA. PBEsol has also been shown to give an improved description of stereoelectronic effects in hydrocarbons.⁶¹

3.4. Performance of Hybrid Density Functionals. Table 3 presents test results for hybrid functionals.

Among the tested hybrid functionals, PWB6K and M05-2X functionals give a good performance, as shown by their small MUEs (0.16 and 0.26 kcal/mol), followed by M06-2X. The best performing hybrid GGA is PBE0, which gives an MUE of 1.49 kcal/mol.

Hybrid functionals have a component of nonlocal Hartree–Fock exchange, thus their computational cost is much higher than the local functionals. In particular, for the HCOOH...benzene complex, the best local functional, M06-L, is about six times faster than the best hybrid functional, PWB6K. PBEsol and SOGGA are even less expensive than M06-L, and they are about eight times faster than PWB6K.

Table 5. M06-L Binding Energies (kcal/mol) with Different Geometries and Basis Sets

method	A	B	C	D	E	MSE ^a	MUE ^b
best estimate	3.15	3.30	4.79	3.23	1.62		
M06-L/DIDZ//M06-L/DIDZ	3.06	3.24	4.65	3.05	1.34	-0.15	0.15
M06-L/6-311+G(2df,2p)//M06-L/6-311+G(2df,2p)	2.87	3.16	4.78	2.89	1.44	-0.19	0.19
M06-L/DIDZ//MP2/6-311+G(2df,2p)	2.91	3.17	4.49	2.98	1.30	-0.25	0.25
M06-L/DIDZ//M06-L/MIDI	2.96	2.84	4.45	2.64	1.38	-0.36	0.36
M06-L/aug-cc-pVTZ//MP2/6-311+G(2df,2p)	2.67	2.99	4.74	2.80	1.00	-0.38	0.38
SOGGA/6-31+G(d)//SOGGA/6-31+G(d)	2.62	2.55	5.36	2.59	1.38	-0.32	0.54
SOGGA/6-311+G(2df,2p)//MP2/6-311+G(2df,2p)	2.47	2.38	4.56	2.53	1.29	-0.57	0.57
PBEsol/6-31+G(d)//PBEsol/6-31+G(d)	2.45	2.41	5.14	2.46	1.26	-0.47	0.61
PBEsol/6-311+G(2df,2p)//MP2/6-311+G(2df,2p)	2.29	2.20	4.30	2.35	1.18	-0.76	0.76

^a MSE denotes mean signed error (same as mean deviation). ^b MUE denotes mean unsigned error (same as mean absolute deviation, MAD).

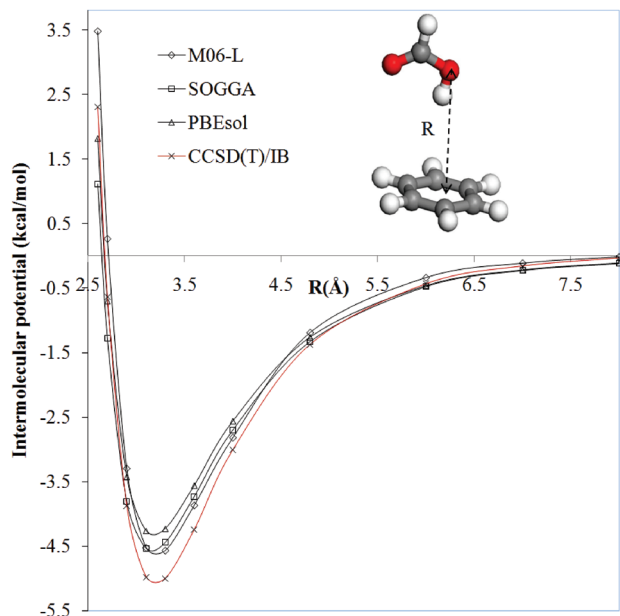


Figure 2. Intermolecular potential of the HCOOH...benzene complex. DFT calculations employed the 6-311+G(2df,2p) basis set without Cp corrections.

3.5. Performance of DFT-D. The results for different DFT-D methods are shown in Table 4. Table 4 confirms the finding in previous studies^{60–63} that empirical dispersion corrections improve the description of noncovalent interactions. All the DFT-D methods in Table 4 have MUEs less than 1.0 kcal/mol. Moreover, the MUE of BLYP-D is about 11 times smaller than that of the original BLYP, showing the effectiveness of the empirical dispersion corrections for the description of noncovalent interactions in HCOOH...benzene complexes. The second best GGA-D method is PBEsol-D. SOGGA-D uses the same empirical dispersion corrections as PBEsol-D, but SOGGA-D gives a slightly larger MUE than PBEsol-D.

3.6. Effects of Geometries and Basis Sets. In previous sections, we based our discussions on single-point energies calculated with the MP2/6-311+G(2df,2p) geometries. In this section, we compare results with the geometries optimized at the M06-L/MIDI!, M06-L/6-31+G(d,p), SOGGA/6-31+G(d), PBEsol/6-31+G(d), and M06-L/6-311+G(2df,2p) levels of theories, where MIDI!⁷¹ is a well-balanced and economical double- ζ basis set for geometry optimization. The results are shown in Table 5.

As shown in Table 5, for a given functional, the effect of geometries and basis sets for the binding energies is small, and they agree with each other within 0.8 kcal/mol. M06-L/6-31+G(d,p) gives a smallest MUE (0.15 kcal/mol), and M06-L/6-31+G(d,p)/M06-L/MIDI! has an MUE of 0.36 kcal/mol. The good performance with the double- ζ quality basis set is likely due to a well-known basis set error that diminishes the underbinding error of an exchange-correlation functional, as shown recently by Ruzsinszky et al.⁷² Similarly, PBEsol/6-31+G(d) gives a better performance than PBEsol/6-311+G(2df,2p).

3.7. Counterpoise Corrected DFT Results. Table 6 presents the Cp corrected binding energies and mean errors. After removing the BSSEs, the best two performers in Table

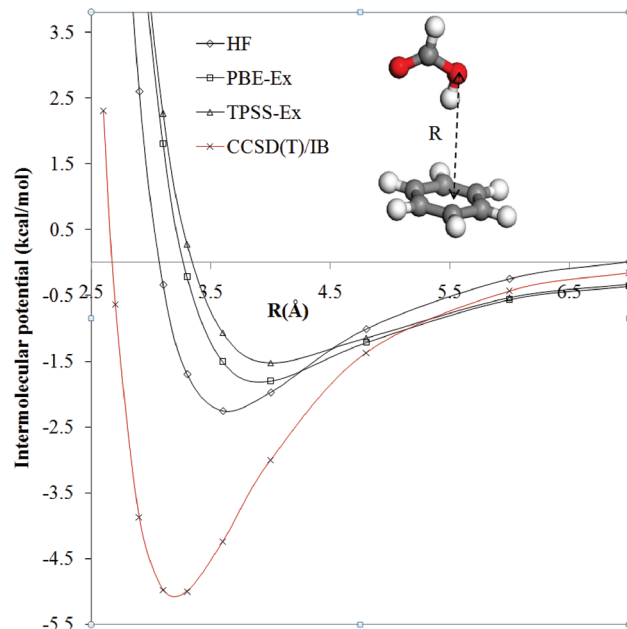


Figure 3. Intermolecular potential of the HCOOH...benzene complex. DFT-Ex and HF calculations employed the 6-311+G(2df,2p) basis set without Cp corrections. The PBE-Ex (PBE exchange-only) calculations were done without PBE correlation contributions using the PBE SCF density. The TPSS-Ex (TPSS exchange-only) calculations were done without TPSS correlation contributions using the TPSS SCF density.

6 are BLYP-D and PBEsol-D, with an MUE of 0.15 kcal/mol. Among the ten best performing functionals, only M05-2X and M06-2X do not have empirical dispersion corrections, and all other eight functionals are DFT-D methods. This result again shows the effectiveness of empirical dispersion corrections and also confirms the finding in Section 3.5.

3.8. Intermolecular Potential of Complex C. We have calculated the intermolecular potential of complex C with the M06-L/6-311+G(2df,2p), PBEsol/6-311+G(2df,2p), SOGGA/6-311+G(2df,2p), and CCSD(T)/IB level of theories, and the intermolecular distance is defined as the distance between the oxygen atom of hydrogen donor in HCOOH and the center of mass of the benzene molecule. The intermolecular potentials are shown in Figure 2.

As shown in Figure 2, the M06-L, PBEsol, and SOGGA intermolecular potential curves show reasonable agreement with that of CCSD(T)/IB. Note that the more accurate CCSD(T)/CBS minimum is above the CCSD(T)/IB minimum by 0.25 kcal/mol, thus shows better agreement with the DFT results. Figure 2 also shows that, even at 5 Å apart, the interaction energy is greater than 1 kcal/mol, which is about twice of the binding energy of neon...benzene van der Waals complex. This result indicates that the interaction between HCOOH and benzene is not just due to dispersion interactions, and the electrostatic contributions play an important role in the HCOOH...benzene complexes.

Results in Figure 2 confirm that GGAs or meta-GGAs, even without empirical dispersion correction, might provide a reasonable description of the noncovalent interactions arising from overlapped nonbonded density. Nevertheless, GGAs or meta-GGAs cannot describe the long-range disper-

Table 6. Counterpoise Corrected Binding Energies and Mean Errors (in kcal/mol)

method ^a	A	B	C	D	E	MSE ^b	MUE ^c
best estimate ^d	3.15	3.30	4.79	3.23	1.62		
BLYP-D	3.10	3.16	4.73	3.19	1.19	-0.15	0.15
PBEsol-D	3.17	3.19	5.16	3.18	1.43	0.01	0.15
ω B97X-D	3.19	3.35	4.61	3.20	1.15	-0.12	0.15
SOGGA-D	3.34	3.37	5.40	3.35	1.55	0.18	0.21
M05-2X	2.85	3.11	4.87	2.96	1.39	-0.18	0.21
M06-2X	3.10	3.58	5.17	3.33	1.35	0.09	0.22
M06-L-D	2.81	3.25	4.85	2.95	1.12	-0.22	0.25
BP86-D	3.22	3.31	5.10	3.33	0.85	-0.06	0.25
BMK-D	3.02	3.31	5.04	3.37	0.80	-0.11	0.27
M06-D	2.74	3.17	4.74	2.87	1.21	-0.27	0.27
B3LYP-D	3.48	3.58	5.22	3.59	1.48	0.25	0.31
PBE-D	3.47	3.57	5.38	3.58	1.58	0.30	0.31
PBE0-D	3.56	3.67	5.49	3.67	1.57	0.37	0.39
TPSS-D	3.72	3.80	5.57	3.80	1.40	0.44	0.53
M06-HF	3.62	4.10	5.68	3.79	1.37	0.50	0.60
PWB6K	2.42	2.51	4.08	2.63	1.41	-0.61	0.61
M06-L/DIDZ//MP2/6-311+G(2df,2p)	2.42	2.65	3.96	2.47	1.02	-0.72	0.72
M06-L/DIDZ/M06-L/MIDI	2.47	2.29	3.92	2.15	1.09	-0.83	0.83
M06-L	2.10	2.44	4.03	2.21	0.89	-0.88	0.88
M06	2.03	2.36	3.92	2.12	0.97	-0.94	0.94
M06-L/aug-cc-pVTZ//MP2/6-311+G(2df,2p)	2.02	2.34	4.01	2.17	0.71	-0.97	0.97
LSDA	4.02	4.29	6.51	4.26	2.24	1.05	1.05
SOGGA	1.94	1.85	3.93	2.01	1.05	-1.06	1.06
BHandH	4.18	4.46	6.43	4.41	2.49	1.18	1.18
PBEsol	1.78	1.67	3.68	1.83	0.94	-1.24	1.24
PW6B95	1.73	1.73	3.26	1.91	1.01	-1.29	1.29
M05	1.37	1.33	2.87	1.49	1.34	-1.54	1.54
B97-1	1.12	0.89	2.47	1.10	0.95	-1.91	1.91
PBE0	1.09	0.85	2.61	1.06	0.75	-1.95	1.95
PBE	0.81	0.55	2.30	0.79	0.70	-2.19	2.19
BMK	0.72	0.69	2.37	0.96	0.04	-2.26	2.26
MPW1K	0.81	0.51	2.24	0.74	0.47	-2.26	2.26
B98	0.74	0.45	2.02	0.68	0.72	-2.30	2.30
MPW3LYP	0.65	0.34	1.89	0.60	0.93	-2.34	2.34
BHandHLYP	0.63	0.32	1.87	0.58	0.76	-2.39	2.39
τ -HCTHh	0.55	0.28	1.93	0.50	0.40	-2.49	2.49
mPW1PW	0.41	0.07	1.79	0.33	0.31	-2.64	2.64
X3LYP	0.30	-0.04	1.52	0.25	0.64	-2.69	2.69
TPSSh	0.34	-0.05	1.64	0.25	0.29	-2.72	2.72
TPSS1KCIS	0.32	-0.07	1.53	0.23	0.43	-2.73	2.73
TPSS	0.18	-0.23	1.46	0.09	0.23	-2.87	2.87
mPWPW91	-0.10	-0.52	1.19	-0.21	0.08	-3.13	3.13
B3LYP	-0.23	-0.64	0.90	-0.32	0.26	-3.23	3.23
B97-2	-0.22	-0.65	0.95	-0.35	0.07	-3.26	3.26
HCTH	-0.52	-1.05	0.44	-0.70	0.74	-3.44	3.44
τ -HCTH	-0.48	-1.06	0.49	-0.70	0.17	-3.53	3.53
BP86	-0.50	-0.92	0.78	-0.57	-0.38	-3.54	3.54
BLYP	-1.15	-1.68	-0.21	-1.27	-0.21	-4.12	4.12
O3LYP	-2.10	-2.89	-1.28	-2.37	-0.49	-5.05	5.05
OLYP	-2.98	-3.89	-2.34	-3.29	-0.88	-5.90	5.90
VSXC	8.76	11.26	12.25	10.35	4.01	6.11	6.11
G96LYP	-3.30	-4.10	-2.53	-3.51	-1.95	-6.30	6.30

^a If basis sets and geometries were not specified, the DFT calculations employed the 6-311+G(2df,2p) basis set and MP2/6-311+G(2df,2p) geometries. ^b MSE denotes mean signed error (same as mean deviation). ^c MUE denotes mean unsigned error (same as mean absolute deviation, MAD). ^d Taken from the CCSD(T)/CBS results of Table 1.

sion interactions in nonoverlapped densities. They give an exponential decay instead of the $-C_6R^{-6}$ behavior for the long-range intermolecular potential.

Table 1 showed that HF theory severely underestimates the interaction energies in the HCOOH...benzene complexes. An interesting observation from Tables 2 and 3 is that some global hybrid functionals (e.g., PBE0 and TPSSh) improve slightly upon corresponding local functionals (e.g., PBE and TPSS). In order to understand the origin of this improvement, we calculated the intermolecular potential with HF theory, PBE-Ex (PBE exchange-only calculation using

the PBE SCF densities), and TPSS-Ex (TPSS exchange-only calculation using TPSS SCF densities). The potential curves are plotted in Figure 3. As shown in Figure 3, for the intermolecular distance at 3–4 Å, HF theory gives more attractive interaction than PBE and TPSS exchange functionals. Thus, replacing certain amount of PBE or TPSS exchange with the HF exchange (as done in PBE0 or TPSSh) results in more attractive interactions at the 3–4 Å region. This explains why PBE0 and TPSSh slightly improve upon the corresponding local PBE and TPSS functionals. Interestingly, PBE and TPSS exchange functionals give more

attractive interactions than HF theory at large intermolecular distance (>4.5 Å), as shown in Figure 3.

4. Conclusions

In the present study, we have employed the MP2 and CCS(T) methods to study structures and interactions in the HCOOH...benzene complexes, and we have developed a benchmark data for binding energies in five noncovalent HCOOH...benzene dimers. The benchmark data were determined as the sum of the complete-basis-set limit of MP2 energies and a CCSD(T) correction term evaluated with the aug-cc-pVDZ basis set. Final binding energies (kcal/mol) are in the range of 1.6–4.8 kcal/mol, and they were used as reference data to test density functionals in the literature. Based on these results, we draw the following conclusions:

1) The small-basis CCSD(T) contributions to the final best estimates of the binding energies are small, with magnitudes in the range of -0.06 to -0.65 kcal/mol.

2) The calculated benchmark data and intermolecular potential are useful for the parametrizations of new force fields and coarse-grained models for chemical species such as the acrylic polymers.

3) The largest binding energy in HCOOH...benzene dimers is 4.8 kcal/mol (complex C), and this binding strength is weaker than that of water dimer but stronger than noncovalent interactions between benzene and first- and second-row hydrides.

4) Among the tested local density functionals without empirical dispersion corrections, M06-L/6-31+G(d,p) gives an MUE of only 0.15 kcal/mol. PBEsol and SOGGA also show promising performance.

5) Empirical dispersion corrections greatly improve the performance of DFT for the descriptions of noncovalent interactions in HCOOH...benzene dimers.

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Supporting Information Available: Cartesian coordinates of the HCOOH...benzene dimers optimized at the MP2/6-311+G(2df,2p) level. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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