J. Phys. Chem. A **2008,** *112,* 6009–6016

Assessment of New Meta and Hybrid Meta Density Functionals for Predicting the Geometry and Binding Energy of a Challenging System: The Dimer of H_2S and Benzene

Hannah R. Leverentz and Donald G. Truhlar*

Department of Chemistry and Supercomputing Institute, University of Minnesota,
Minneapolis, Minnesota 55455-0431

Received: March 2, 2008; Revised Manuscript Received: April 7, 2008

Noncovalent interactions of a hydrogen bond donor with an aromatic π system present a challenge for density functional theory, and most density functionals do not perform well for this kind of interaction. Here we test seven recent density functionals from our research group, along with the popular B3LYP functional, for the dimer of H_2S with benzene. The functionals considered include the four new meta and hybrid meta density functionals of the M06 suite, three slightly older hybrid meta functionals, and the B3LYP hybrid functional, and they were tested for their abilities to predict the dissociation energies of three conformations of the H_2S−benzene dimer and to reproduce the key geometric parameters of the equilibrium conformation of this dimer. All of the functionals tested except B3LYP correctly predict which of the three conformations of the dimer is the most stable. The functionals that are best able to reproduce the geometry of the equilibrium conformation of the dimer with a polarized triple-ζ basis set are M06-L, PWB6K, and MPWB1K, each having a mean unsigned relative error across the two experimentally verifiable geometric parameters of only 8%. The success of M06-L is very encouraging because it is a local functional, which reduces the cost for large simulations. The M05-2X functional yields the most accurate binding energy of a conformation of the dimer for which a binding energy calculated at the CCSD(T) level of theory is available; M05-2X gives a binding energy for the system with a difference of merely 0.02 kcal/mol from that obtained by the CCSD(T) calculation. The M06 functional performs well in both categories by yielding a good representation of the geometry of the equilibrium structure and by giving a binding energy that is only 0.19 kcal/mol different from that calculated by CCSD(T). We conclude that the new generation of density functionals should be useful for a variety of problems in biochemistry and materials where aromatic functional groups can serve as hydrogen bond acceptors.

1. Introduction

To accurately and inexpensively model systems of noncovalently bound molecules is an ongoing challenge for computational chemists.[1,2] Coupled cluster theory with single and double excitations and quasiperturbative connected triple excitations (CCSD(T))[3] is an ab initio computational method that is generally thought to be capable of accurately predicting the energies of a wide variety of systems including the energies of binding for noncovalently bound molecules, but it is usually too expensive to apply to systems containing more than 10 or 15 atoms. Other wave function-based correlated methods, such as second- and higher-order Møller−Plesset perturbation theory (MP2,[4] MP4,[5] etc.) become impractical for very large systems and are too expensive for full simulations even for many smaller systems. On the other hand, methods that are based on density functional theory (DFT) are much less computationally expensive and can be used on systems containing thousands of atoms, but, until recently, available density functionals were incapable of describing dispersion-like interactions without empirical parametrization or a fortuitous cancelation of errors.[6,7]

However, the situation is not so bleak as it once appeared, and "it would be an oversimplification to dismiss DFT methods for noncovalent interaction in general."[7] Recent work has shown that one can design functionals that capture the medium-range dispersion-like interactions and the electrostatic, induction, and charge-transfer interactions that determine the binding energies of van der Waals molecules and the strengths of hydrogen bonds.[2,7–9] One must be able to treat all four of these kinds of attractive interactions accurately for problems such as the competition[2,10] between π−π stacking (dominated by medium-range dispersion-like interactions) and conventional hydrogen bonding (dominated by the other three). Density functional methods have been used to calculate interaction energies for a variety of hydrogen-bonded systems, ranging from "true" hydrogen bonds (H−O···H−O, H−N···H−N, etc.) to "pseudo"-hydrogen bonds, such as O−H···π and S−H···π, where "π" refers to the π system, especially one in an aromatic ring.[7,11–16] The accuracy of the result of a binding energy calculation on a hydrogen-bonded system of any kind may vary drastically with the density functional chosen to perform the calculation.[11,17] Ideally one would hope to find a single density functional that works well for the entire range of hydrogen bond types, from the strong short-range "true" hydrogen bonds such as those found in water to weaker, longer-range pseudo-hydrogen bonds such as those found between second-row hydrides and the π system of an aromatic ring. Such a functional would prove invaluable for the computational modeling of protein folding and protein crystal packing because a variety of hydrogen bond types, including both stronger and weaker hydrogen bonds, play essential roles in these processes;[18–20] such noncovalent interactions may also be important in protein−carbohydrate interactions, carbon nanotubes, materials built with fullerenes and graphene sheets, and conducting polymers.

---

* To whom correspondence should be addressed. Corresponding author fax: 612-624-9390; email: truhlar@umn.edu.

10.1021/jp8018364 CCC: $40.75

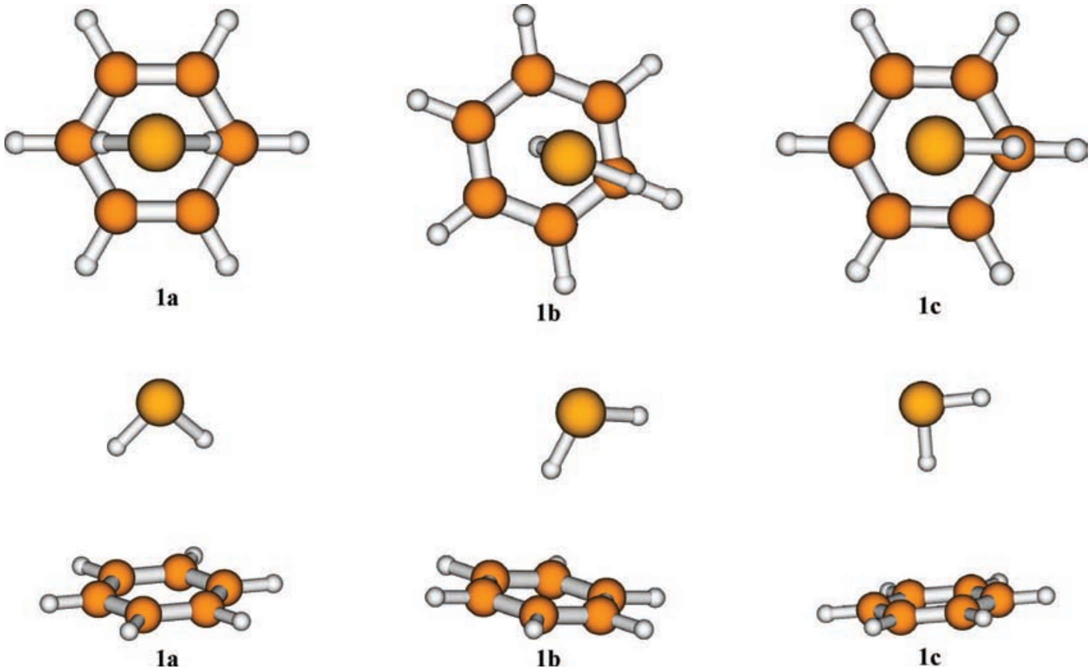

Figure 1. Input structures used for DFT optimizations of the H_2S−benzene dimer (adapted from Figure 1 of ref 16). The top row gives views from above, and the bottom row gives views from the side. Structure **1a** has C_{2v} symmetry. Structure **1b** has C_s symmetry, with an S−H−C bond angle of ~180°. Structure **1c** has C_s symmetry with one of the H−S bonds of H_2S pointing to the center of the benzene ring.

Previous studies[7,15,17] have demonstrated the ability of several newly developed meta and hybrid meta density functionals to accurately predict the interaction energies of shorter-range hydrogen bonds and even of longer-range hydrogen bonds between first-row hydrides and an aromatic ring. Wang and Paulus[16] recently tested 11 density functionals for their abilities to predict the binding energy of an even weaker and longer-range hydrogen bond: the interaction between a second-row hydride and an aromatic ring that occurs in the H_2S−benzene dimer. This particular interaction (i.e., the relatively weak $S-H\cdots\pi$ interaction) is of interest because it makes a noteworthy contribution to the stability of the conformations of certain folded proteins[20,21] and because it could potentially be the basis for the creation of an H_2S sensor composed of single-walled carbon nanotubes (SWCNTs).[16] The present study puts the newly developed density functionals that are recommended in previous work[7,15,17] as being the best for hydrogen bonds (and for noncovalently bound systems in general) to a test similar to that posed by Wang and Paulus in order determine whether or not these newer functionals capably reproduce the dissociation energies and the geometries of three bound conformations of the H_2S−benzene dimer and thus (because these density functionals have already performed well on shorter and middle-range hydrogen bonds) demonstrate their ability to qualitatively describe an entire array of possible hydrogen bond types.

2. Computational Details

Wang and Paulus[16] determined three bound conformations of the H_2S−benzene dimer by fully optimizing several possible geometries of the dimer at the MP2 level of theory with the aug-cc-pVXZ (where X = D, T, and Q)[22,23] and 6-311++G(d,p)[24] basis sets. The structures of these three conformations are shown in Figure 1 and have been used as the input structures for full optimization and frequency calculations in the present work by using the recently developed density functionals recommended[7,15,17] for hydrogen-bonded systems. The structures of the three bound conformations are named in accordance with those assigned by Wang and Paulus: **1a** denotes a structure with C_{2v} symmetry wherein the sulfur atom is located directly above benzene's center of mass and the two hydrogen atoms of H_2S are in a plane determined by the C_6 axis of benzene and a line directly through two opposite carbon atoms of the benzene ring. The **1b** and **1c** structures both have C_s symmetry; in the **1b** structure the angle formed by the sulfur atom, one of the hydrogen atoms of H_2S, and one of the carbon atoms of benzene is nearly 180°, whereas in the **1c** structure that hydrogen atom points almost directly to benzene's center of mass.

The dissociation energies of the H_2S−benzene dimer given in this paper and in the paper by Wang and Paulus were calculated as

$$D_e = -E(\mathrm{D}) + E(C_6H_6) + E(H_2S) \qquad (1)$$

where E is the electronic energy (including nuclear repulsion), D is the gas-phase H_2S−benzene dimer, C_6H_6 is the gas-phase benzene monomer, and H_2S is the gas-phase H_2S monomer. In most of the calculations done for this paper, both of the monomers and the dimer were fully optimized at a given level of theory and with a given basis set in order to determine E(D), $E(C_6H_6)$, and $E(H_2S)$. We use the notation L/B to indicate a calculation that was fully optimized at level of theory L and basis set B. In some cases, however, each term in eq 1 was not fully optimized. For those cases we use the notations L1/B1//L2/B2 and L/B/d. The notation L1/B1//L2/B2 means that a full optimization was done at the level of theory L2 with basis set B2 to obtain a reasonable geometry for the dimer and that this geometry was then used to perform a single-point energy calculation at level of theory L1 with basis set B1. L/B/d indicates that the energy of the dimer was optimized with respect to only a single coordinate, d. For both of these cases (i.e., those cases in which either the notation L1/B1//L2/B2 or the notation L/B/d is used) the monomer geometries were not optimized at any level of theory but were taken to have the structural parameters listed in Table 1, which are the best literature values

TABLE 1: Best Literature Values for the Structural Parameters of the H_2S and Benzene mMonomers

H_2S monomer[a]	
S−H bond length	1.3356 Å
H−S−H bond angle	92.12°
benzene monomer[b]	
C−C bond length	1.3915 Å
C−H bond length	1.0800 Å

[a] From ref 41. [b] From ref 40.

currently available for the true equilibrium geometries of the H_2S and benzene monomers.

The eight density functionals tested in this study are the hybrid meta GGA functionals PWB6K,[25] M05-2X,[9] M06,[15] M06-2X,[15] M06-HF,[26] and MPWB1K,[17] the meta GGA functional M06-L,[27] and the hybrid GGA functional B3LYP.[28] The MPWB1K and PWB6K functionals were selected because they have already shown good performance for systems wherein the hydrogen of a first-row hydride (such as water or NH_3) or even the hydrogen of HCl are noncovalently bound to the π network of an aromatic ring.[7,29] These two functionals have also performed well in studies testing their ability to find the dissociation energies of a variety of other noncovalently bound systems.[2,29–31] Previous research[2,15,27,32,33] has shown that the relatively new M05-2X, M06, M06-2X, M06-L, and M06-HF functionals give good results (compared to other density functionals of their respective kinds; i.e., the meta GGA functional listed does well compared to older meta GGA and GGA functionals but not necessarily as well as older hybrid or hybrid meta functionals) for various types of noncovalent interactions, including hydrogen bonding and even, in some cases, $\pi-\pi$ stacking and have therefore been chosen for further testing in this study. The B3LYP functional was included in this study because, even though it is an older functional, it is still by far the most widely used functional in a variety of applications. The basis set used for all but three of the optimization and single-point energy calculations done for the present study was the MG3S basis, which for hydrogen is the same as 311G(2p), for carbon is 6-311+G(2df), and for sulfur is an improved version[34] of 6-311+G(3d2f). The aug-cc-pVTZ basis set was used in conjunction with the MPWB1K functional to perform geometry optimization calculations on the three conformations of the H_2S−benzene dimer for comparison with the Wang and Paulus study.

The Gaussian 03 software package[35] in conjunction with the Minnesota Gaussian Functional Module (MN-GFM)[36] was employed to carry out all optimization and single-point energy calculations done in the present study. The counterpoise correction[37] (CP) for basis set superposition error (BSSE) was not added to any of the DFT energies calculated for the present study, although such a correction was added for some of the energies of the H_2S−benzene dimer in the other references cited in this work. Whether or not the counterpoise correction for BSSE was used to compute an energy value listed in this work will be clearly indicated near the energy value wherever it is presented, be it in the body of the text or in a table.

3. Results and Discussion

3.1. Dissociation Energies of the Three Bound Conformations of the H_2S−Benzene Dimer Predicted by DFT Calculations Compared to Those Predicted by MP2 Calculations.

The dissociation energies (D_e) of the noncovalent interaction energies between benzene and H_2S in each of the three bound dimer conformations were determined by Wang and Paulus to be 3.63, 3.70, and 3.75 kcal/mol for structures **1a**−**c**, respectively, after full optimizations at the MP2 level of theory with the aug-cc-pVQZ basis set and with counterpoise correction for BSSE.[16] For the present study, the dissociation energies of these conformations were calculated by several more recently developed density functionals. These dissociation energies, along with some of those calculated by Wang and Paulus and others calculated by Tauer et al. in a separate study,[20] are presented in Table 2.

The “CP?” column of Table 2 indicates whether or not a counterpoise correction for BSSE was included in the calculation of the dissociation energy; a “Y” in this column denotes that yes, counterpoise correction was used, whereas an “N” denotes that counterpoise correction was not used.

The “MSD (MP2)” column of Table 2 denotes the mean signed deviation across all three conformers between the dissociation energies calculated at the given level of theory and basis set and the dissociation energies calculated with MP2/aug-cc-pVQZ. A negative value in this column indicates that on average the given level of theory and basis set predicted lower dissociation energies for the conformers than those that were predicted at MP2/aug-cc-pVQZ. The reader must note that this column should not necessarily be taken as the best measure of the accuracy of the binding energies calculated at the various levels of DFT; a better measure of this kind of accuracy will be discussed in section 3.3. The reasons the dissociation energies of the conformers calculated by MP2 may not be the best benchmark will be more clear after sections 3.2 and 3.3, but we summarize three of those reasons here: (1) Although MP2 does a good job of predicting geometries of various conformers (see section 3.2), the lowest-energy conformer predicted by MP2 is **1c**, whereas experimentally observed conformations of the H_2S−benzene dimer[38] and the similar water−benzene dimer[39] are best represented by **1b**, so it would appear from experiment that the most stable conformer of the H_2S−benzene dimer is really **1b**. (2) Compared to CCSD(T) calculations done on the three bound dimer conformations, MP2 overestimates the dissociation energy by nearly 1 kcal/mol. (3) MP2 is well-known to suffer from large basis-set superposition error. For those three reasons, the MSD (MP2) column should be seen as a bookkeeping column that displays a measure of how much each level of theory tends to “bind” the three dimers; for example, with a negative MSD (MP2) of −1.98 kcal/mol, one can see that MPWB1K/MG3S predicts that none of the three conformers will be strongly bound, whereas at the positive MSD of 1.50 kcal/mol for MP2/aug-cc-pVDZ shows that this method results because MP2 predicts too much binding.

The newer density functionals tested in this study all predict that the three conformers of the H_2S−benzene dimer are more weakly bound than MP2 calculations suggest, but that they are more strongly bound than a B3LYP calculation predicts. Also, MP2 calculations done with or without counterpoise correction for BSSE and with any of the Dunning (aug-cc-pVXZ) basis sets predict that the **1c** conformer is the most stable, followed by **1b** and last by **1a**, whereas every density functional tested in this study (with the exception of B3LYP, which will be discussed later in this section) predicts that **1b** is the most stable conformer. Frequency analysis of the optimal **1b** conformation by each density functional show that four functionals, M06-2X, M06, M06-HF, and M05-2X yield the **1b** conformation as a local minimum on the potential energy surface (PES) for the H_2S-benzene dimer. On the other hand, PWB6K, M06-L, and MPWB1K/MG3S all classify the **1b** conformer as a hilltop or

TABLE 2: Dissociation Energies (kcal/mol) of the Three Bound H_2S−Benzene Dimer Conformations

method/basis set	ref[d]	CP?	D_e(**1a**)	D_e(**1b**)	D_e(**1c**)	MSD (MP2)
B3LYP/MG3S	P	N	0.47	N/A[c]	0.71	N/A
MPWB1K/MG3S	P	N	1.57	2.00	1.58	−1.98
MPWB1K/aug-cc-pVDZ	P	N	2.14	2.36	1.73	−1.62
MPWB1K/aug-cc-pVDZ	16	N	2.14	2.37	2.38	−1.40
MPWB1K/aug-cc-pVDZ	16	Y	1.76	1.91	N/A	N/A
PWB6K/MG3S	P	N	2.01	2.49	1.93	−1.55
M05-2X/MG3S	P	N	2.81	2.97	2.87	−0.81
M06-L/MG3S	P	N	1.80	2.56	1.69	−1.68
M06-HF/MG3S	P	N	3.12	3.51	3.40	−0.35
M06/MG3S	P	N	1.71	2.70	1.49	−1.73
M06-2X/MG3S	P	N	3.17	3.34	3.12	−0.48
MP2/aug-cc-pVDZ	16	N	5.05	5.16	5.36	1.50
MP2/aug-cc-pVDZ	16	Y	2.97	3.03	3.05	−0.68
MP2/aug-cc-pVDZ/*d*	20	Y	3.06	N/A	N/A	N/A
MP2/aug-cc-pVTZ	16	N	4.38	4.52	4.61	0.81
MP2/aug-cc-pVTZ	16	Y	3.45	3.53	3.60	−0.17
MP2/aug-cc-pVTZ/*d*	20	Y	3.47	N/A	N/A	N/A
MP2/aug-cc-pVQZ	16	N	3.98	4.05	4.15	0.37
MP2/aug-cc-pVQZ	16	Y	3.63	3.70	3.75	0.00
MP2/aug-cc-pVQZ/*d*	20	Y	3.60	N/A	N/A	N/A
CCSD(T)/aug-cc-pVTZ/(inc.)[a]	16	Y	2.73	2.69	N/A	N/A
CCSD(T)/aug-cc-pVTZ/*d*	20	Y	2.64	N/A	N/A	N/A
CCSD(T)/aug-cc-pVQZ// CCSD(T)/aug-cc-pVTZ/*d* (est.)[b]	20	Y	2.74	N/A	N/A	N/A
CCSD(T)/CBS limit//CCSD(T)/aug-cc-pVTZ/*d*[c]	20	Y	2.81	N/A	N/A	N/A

[a] This calculation was not a full CCSD(T) optimization but was obtained by the method of increments; see ref 16 for details. [b] This calculation was an estimate of the CCSD(T)/aug-cc-pVQZ based on a full optimization done at MP2/aug-cc-pVQZ and CCSD(T)/aug-cc-pVTZ/*d* calculation. See ref 20 for details. [c] See section 3.1 for an explanation. [d] The "ref" column gives the number of the reference from which the dissociation energy values were taken; a "P" in this column indicates that the calculation was done in the present study.

a saddle point, with 2, 1, and 2 imaginary frequencies, respectively. B3LYP does not yield the **1b** conformation as a stationary point of any kind; none of the B3LYP geometry optimizations converged to a **1b** conformation of the dimer.

Of the eight density functionals assessed with the MG3S basis set in this work, four predict that **1c** is the least stable conformer and four predict that **1a** is the least stable conformer. All four functionals that predict **1b** to be the most stable conformer and **1c** to be the least stable (PWB6K, M06-2X, M06, and M06-L) agree that the **1b** conformer is much more stable than either **1a** or **1c**; that is, those four functionals all agree that the dissociation energy of the **1a** conformer is much closer that of the **1c** conformer than it is to that of the **1b** conformer. No such clear trend exists among the four density functionals (B3LYP, M06-HF, M05-2X, and MPWB1K) that predict **1b** to be the most stable conformation of the dimer and **1a** to be the least stable. M05-2X and MPWB1K predict that **1c** is closer in energy to **1a** than to **1b**, but B3LYP and M06-HF predict that **1c** is closer in energy to **1b** than to **1a**. The reason B3LYP places the D_e of **1c** so close to that of **1b** becomes obvious when one visualizes the structures; even when the **1b** structure is used as the starting point for a geometry optimization by B3LYP, the result of the optimization is a structure that looks just like **1c**, with a hydrogen−sulfur bond pointing almost directly to the center of the benzene ring. M06-HF, however, does locate a minimum on the PES for the H_2S−benzene dimer that has the **1b** structure and still predicts that the **1c** conformer will be closer in energy to that **1b** conformer than to the **1a** conformer.

The dissociation energies calculated at the MPWB1K/aug-cc-pVDZ level (without correction for BSSE) for the **1b** and **1c** conformers in the present study disagree with those calculated (also without correction for BSSE) with the same functional and basis set by Wang and Paulus. For the **1b** conformer, this discrepancy is nearly negligible: Wang and Paulus found the D_e of this conformer to be 2.37 kcal/mol, and the present study found it to be 2.36 kcal/mol. However, section 3.2 will show that the geometries predicted at this level of theory by the two studies for the **1b** conformer may be quite different. For the **1c** conformer, the discrepancy between the dissociation energy values is significant: Wang and Paulus get a value of 2.38 kcal/mol, whereas we obtained a value of 1.73 kcal/mol. Clearly this affects the relative stabilities predicted for the three conformations of the dimer: the Wang and Paulus study showed that MPWB1K/aug-cc-pVDZ without correction for BSSE predicts that **1c** is the most stable conformer, followed by **1b** and finally by **1a** as the least stable conformer. The present study finds that what should be the same calculation predicts **1b** to be the most stable conformer, followed by **1a** and finally **1c**. One possible explanation for these differences is that different input structures were used in each study for the geometry optimizations. Both studies used structures that fit the symmetry and other general structural requirements given in Figure 1, but parameters such as bond lengths and tilt angles were not exactly the same. Perhaps the region of the PES that incorporates all H_2S−benzene geometries that could be classified as **1c** conformers is relatively flat and contains several shallow minima or stationary points. We note that our own studies used tight SCF convergence parameters, and all structures are well-converged.

3.2. Geometry of the 1b Conformation of the H_2S−Benzene Dimer Predicted by DFT Compared to That Obtained by Experiment. Prior to the publication of the theoretical work done by Wang and Paulus on the gas-phase H_2S−benzene dimer, an experimental study on this dimer had been performed by Arunan et al.[38] The equilibrium geometry of the dimer was found to have a structure similar to that of **1b** in Figure 1, with a distance of 3.818 Å between the sulfur atom and benzene's center of mass and with an angle of 28.5° between the C_{2v} axis of H_2S and approximately the C_6 axis of benzene. (The "approximately" modifier is added because the angle measured in the experiment was actually the angle between the C_{2v} axis of H_2S and the "*a*" axis of the dimer; fortunately, the

TABLE 3: Key Structural Parameters of the 1b Conformation of the H_2S−Benzene Dimer

method/basis set	ref[a]	**1b** angle (deg)	d (Å)	Δ(S−H)(Å)	Δ(HSH) (deg)	SHC angle (deg)
PWB6K/MG3S	P	23.2	3.87	0.002	−0.4	180
MPWB1K/MG3S	P	23.6	3.89	0.002	−0.5	180
MPWB1K/aug-cc-pVDZ	P	23.7	3.83	0.002	−0.3	179
MPWB1K/aug-cc-pVDZ	16	16	3.83	0.002	−0.5	170
M05-2X/MG3S	P	20.0	3.78	0.003	−0.3	177
M06-L/MG3S	P	24.4	3.79	0.003	−0.2	179
M06-HF/MG3S	P	19.6	3.65	0.004	−0.4	178
M06/MG3S	P	23.2	3.84	0.004	−0.3	176
M06-2X/MG3S	P	19.0	3.70	0.003	−0.4	178
MP2/aug-cc-pVDZ	16	27	3.63	0.004	−1.1	179
experimental	38	28.5	3.82	N/A	N/A	N/A

[a] The "ref" column gives the number of the reference from which the values were taken; a "P" in this column indicates that the values were obtained in the present study.

TABLE 4: Errors between Calculations and Experiment for Key Structural Parameters of the 1b Conformation of the H_2S−Benzene Dimer

method/basis set	ref[a]	error in **1b** angle (deg)	error in d (Å)	MUPE[b]
PWB6K/MG3S	P	−5.3	0.06	8
MPWB1K/MG3S	P	−4.9	0.07	8
MPWB1K/aug-cc-pVDZ	P	−4.8	0.02	8
MPWB1K/aug-cc-pVDZ	16	−12.5	0.01	22
M05-2X/MG3S	P	−8.5	−0.04	15
M06-L/MG3S	P	−4.1	−0.03	8
M06-HF/MG3S	P	−8.9	−0.17	18
M06/MG3S	P	−5.3	0.02	9
M06-2X/MG3S	P	−9.5	−0.11	18
MP2/aug-cc-pVDZ	16	−1.5	−0.19	5
experimental[c]	38	0.0	0.00	0

[a] The "ref" column gives the number of the reference from which the values were taken; a "P" in this column indicates that the values were obtained in the present study. [b] Mean unsigned percent error. See section 3.2 for an explanation of how the values in this column were obtained. [c] The **1b** angle is 28.5°; d is 3.818 Å.

a axis of the dimer happened to almost exactly coincide with the C_6 axis of benzene.) This geometry was used as the standard against which the geometry predicted by each density functional for the **1b** conformation was compared. Because B3LYP did not predict any geometry for a **1b** conformation of this dimer as explained in section 3.1, no B3LYP data have been included in Tables 3 and 4.

Table 3 presents a few of the key structural parameters of the **1b** conformation of the H_2S−benzene dimer. The "**1b** angle" refers to the angle (in degrees) formed between the C_6 axis of benzene and the C_{2v} axis of H_2S in the **1b** conformer. The distance "d" is the distance in angstroms between the sulfur atom and benzene's center of mass. Not surprisingly, the density functionals that predicted higher dissociation energies for the dimer also predict shorter d values. The "Δ(S−H)" and the "Δ(HSH)" columns give the predicted distortions in the length of the S−H bond (in angstroms) and the HSH bond angle (in degrees) as the H_2S molecule goes from being the gas-phase monomer to forming a hydrogen bond with benzene's π system in the **1b** conformation. That all the values in the Δ(S−H) column are positive and that all the values in the Δ(HSH) column are negative indicate that every density functional tested predicts that the S−H bond is stretched and that the H−S−H bond angle is compressed in the complex. The "SHC angle" column gives the angle (in degrees) formed between the sulfur atom, the hydrogen atom closest to the benzene molecule, and the nearest carbon to that hydrogen on the benzene molecule.

Table 4 enables one to see how accurately each method is able to reproduce the experimentally determined geometry of the **1b** conformation of the H_2S−benzene gas-phase dimer. A negative value in either column indicates that the theoretically predicted value is less than the experimental value, whereas a positive value implies that the theoretically predicted value is greater than the experimental value. The "MUPE" column lists the mean unsigned percentage errors across the two key experimentally verifiable structural parameters for the **1b** conformation of the dimer; that is, the values in this column were calculated by averaging the unsigned percent error in the **1b** angle and the unsigned percent error in d.

Table 4 shows that, even with a polarized double-ζ (i.e., smaller) basis set, MP2 is the method that most accurately predicts the key structural parameters of the **1b** conformer with an MUPE of 5%. With a polarized triple-ζ (larger) basis set, three of the density functionals are able to do nearly as well as MP2 did with the polarized double-ζ basis: MPWB1K, PWB6K, and, encouragingly because it is a meta-GGA functional, M06-L, each having an MUPE of only 8%. M06 also does well with an MUPE of 9%. Even though a larger basis set was needed in order to achieve these levels of accuracy for the density functionals, the computational cost was still quite low: most of the full geometry optimizations took only a few hours to complete on a single processor with 600 Mbytes of memory. The exception to this was B3LYP, which never converged to a **1b** conformation of the dimer.

A discrepancy exists between the structural parameters predicted by MPWB1K with the polarized double-ζ basis set (aug-cc-pVDZ) calculated by Wang and Paulus and those calculated for the present study with the same density functional and basis set: the result of Wang and Paulus' calculation gave a **1b** angle of only 16° and an overall MUPE of 22%, whereas this study found that angle to be 23.7°, quite a bit closer to the experimental value and therefore with a much better MUPE of 8%. We already mentioned, in discussing Table 2, that the D_e value for the **1b** conformer calculated by Wang and Paulus does not match the D_e value calculated for the **1b** conformer in the present study. This may indicate that two different structures, both of which are quite close in energy and can be classified as "**1b** conformers" with C_s symmetry and an SHC angle of nearly 180°, are stationary points on a PES generated by a series of MPWB1K/aug-cc-pVDZ calculations.

3.3. Binding Energy of a 1a Conformation of the H_2S−Benzene Dimer Compared to That Calculated by CCSD(T).

Tauer et al. have also previously explored the energy of binding of the H_2S−benzene dimer in a theoretical study.[20] Tauer et al. desired to find the lowest-energy conformation of this dimer using the highest level of electronic structure theory available both then and now: CCSD(T). The great computational

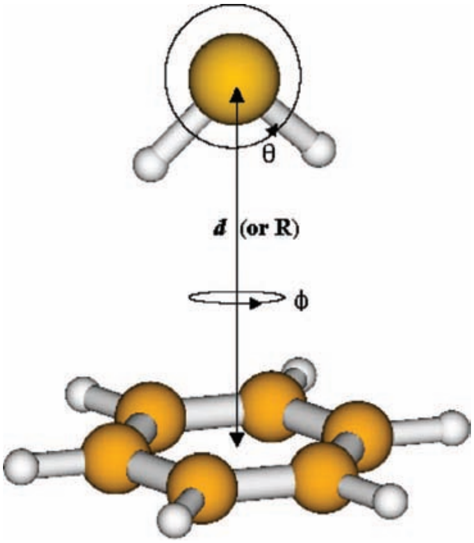

Figure 2. Coordinates varied in a partial optimization of the **1a** conformation of the H_2S−benzene dimer at the CCSD(T) level of theory. See section 3.3 and ref 20 for definitions of the coordinates.

expense of this method unfortunately precluded (and still precludes) a full optimization of this system with an adequate basis set, so Tauer et al. instead did several series of single-point energy calculations using CCSD(T) with aug-cc-pVDZ and aug-cc-pVTZ basis sets on various geometries of the dimer. These calculations included the counterpoise correction for BSSE. In each series of single-point energy calculations, Tauer et al. held all general coordinates of the molecule fixed but one; this one coordinate was varied over its entire range of reasonably possible values, and the minimum energy with respect to that coordinate was determined. Ultimately three general coordinates of the dimer were varied one at a time: the "swing" angle θ, the "twist" angle ϕ, and the intermonomer distance d between the sulfur atom and benzene's center of mass (see Figure 2 of this paper or Figure 1 of ref 20; the distance d in this work is equivalent to the distance R in ref 20, θ is equivalent to A1, and ϕ is equivalent to A2). It was determined that varying ϕ made a less than 0.01 kcal/mol difference in the various energies of binding the dimer, so for simplicity this angle was left at 0° for all subsequent calculations. Varying the swing angle θ showed that the lowest binding energy was reached at an angle of about 30°, but because this minimum was only 0.06 kcal/mol lower than the saddle point at 0°, θ was also set at 0° for the remaining calculations. Finally, with the monomers frozen at their literature values given in Table 1 and in refs 40 and 41 and with θ and ϕ set at 0°, the intermolecular distance d was varied from 3.00 to 7.00 Å. The value of d that yielded the strongest binding at the CCSD(T)/aug-cc-pVTZ level was 3.80 Å. The energy of binding of this dimer, which looks like the **1a** dimer shown in Figure 1, was calculated as

$$\mathrm{BE(a)} = E(\mathrm{D,a}) - E(\mathrm{C_6H_6}) - E(\mathrm{H_2S}) \qquad (2)$$

where in this case E(D,a) is the electronic energy of the **1a** dimer with the structural parameters given above, and $E(C_6H_6)$ and $E(H_2S)$ are the electronic energies of the monomers with the structural parameters given in Table 1. The energy of binding for this particular geometry of the dimer was extrapolated to the complete basis set (CBS) limit, and this best estimate for the energy of binding of this system was found to be −2.81 kcal/mol. BE(a) was calculated according to eq 2 by each of the density functionals included in this study and each value was compared to the best estimate of BE(a) = −2.81 kcal/mol from Tauer et al. These results are displayed in Table 5.

TABLE 5: Binding Energies for a Specific Geometry[a] of the 1a Conformation of the H_2S−Benzene Dimer

method/basis set	ref[b]	CP?	BE(a) (kcal/mol)	error (kcal/mol)	% error
B3LYP/MG3S//b	P	N	−0.01	2.80	100
MPWB1K/MG3S//b	P	N	−1.76	1.05	37
PWB6K/MG3S//b	P	N	−2.28	0.53	19
M05-2X/MG3S//b[c]	P	N	−2.79	0.02	1
M06-L/MG3S//b	P	N	−2.44	0.37	13
M06-HF/MG3S//b	P	N	−3.01	−0.20	−7
M06/MG3S//b	P	N	−2.62	0.19	7
M06-2X/MG3S//b	P	N	−3.06	−0.25	−9
MP2/MG3S//b	P	N	−3.79	−0.98	−35
Best Estimate[d]	20	Y	−2.81	0.00	0

[a] See section 3.3 for a description of this geometry. [b] The "ref" column gives the number of the reference from which the values were taken; a "P" in this column indicates that the values were obtained in the present study. [c] b = CCSD(T)/aug-cc-pVTZ/*d*. See sections 2 and 3.3 for an explanation of this notation. [d] CCSD(T)/CBS limit//CCSD(T)/aug-cc-pVTZ/*d*. See section 3.3 for a summary of the origin of these values, and see ref 20 for details.

In Table 5, the "BE(a)" column lists the binding energy for the dimer calculated according to eq 2. The "error" column is the BE(a) value (kcal/mol) calculated at the given level of theory minus our best estimate of −2.81 kcal/mol, which is the BE(a) value for the same system calculated by Tauer et al. as described above and in ref 20. The "% error" column is the error column value at the same level of theory divided by the absolute value of the best estimate of BE(a). In both of those columns a negative value implies that the given level of theory "overbinds" the dimer (i.e., the level of theory yields a BE(a) that is too negative relative to the best estimate) and a positive value implies that the level of theory "underbinds" the dimer.

With an error of 0.02 kcal/mol and a relative error of merely 1%, the M05-2X density functional is clearly able to closely reproduce the best estimate of the binding energy of this specific geometry of the **1a** conformation of the H_2−benzene dimer. Three other functionals also did quite well: M06, M06-HF, and M06-2X, with errors of only 0.19, −0.20, and −0.25 kcal/mol and relative errors of 7, −7, and −9%, respectively. Every density functional tested, with the exceptions of B3LYP and MPWB1K, was able to calculate a significantly more accurate binding energy for this system than MP2 with the same basis set. MP2 overbound the system by 0.98 kcal/mol for a large relative error of −35%, whereas the remaining functionals (excluding the two exceptions noted earlier) all achieved absolute relative errors of less than 20% (which would correspond to an absolute error of less than 0.56 kcal/mol). MPWB1K performed only slightly worse than MP2 with an error of 1.05 kcal/mol and a relative error of 37%, but the popular B3LYP significantly underbound the system with an error of 2.80 kcal/mol and therefore a relative error of 100%.

4. Conclusions

To obtain accurate dissociation energies and geometries for weakly hydrogen-bonded systems is a difficult task for any electronic structure method and especially for density functional theory. The goal of this work was to determine whether or not several relatively new meta and hybrid meta density functionals would be able to capture most of the noncovalent interaction energy of such a system and also to see whether or not they would be able to accurately reproduce the geometry of such a system. The prototypical weakly hydrogen-bonded system chosen for this study was the H_2S−benzene dimer, which involves of a weak hydrogen-bond interaction between a second-row hydride and the conjugated π system of the benzene ring. The density functionals were used to optimize the geometries of three conformations of this dimer (**1a**, **1b**, and **1c** shown in Figure 1) and to find the dissociation energy of each of the three conformations. MP2 optimizations done on the three conformations with various basis sets all predict that the **1c** conformation of this dimer is the most stable; however, every density functional tested in this study (with the exception of B3LYP) predicts that the **1b** conformation of the dimer is the most stable. The results of the dissociation energy calculations by the density functionals appear to be more qualitatively accurate than those obtained from MP2, because an experimental study on this dimer with microwave spectroscopy implies that the equilibrium geometry of the dimer is best classified as the **1b** conformation.[38] MP2, even with only a polarized double-ζ basis set, does do an excellent job of reproducing the geometry of this equilibrium structure, but several of the density functionals when used with a polarized triple-ζ basis do nearly as well as MP2 with the polarized double-ζ, and still at a low computational cost. The density functionals that were able to most closely reproduce the equilibrium geometry (i.e., the **1b** conformation) of the dimer when used with the MG3S basis set were the meta-GGA functional M06-L and the hybrid meta functionals MPWB1K and PWB6K. The hybrid meta functional M06 was also able to reproduce key structural parameters of the **1b** conformer reasonably well with a mean unsigned percent error of less than 10%. The quantitative accuracy of the density functionals' calculations of the dissociation energy of a particular **1a** conformation of the dimer was tested by comparing each functional's result for the dissociation energy of the dimer with the dissociation energy calculated at the CCSD(T) level and extrapolated to the limit of an infinite basis set. The density functional that yielded the greatest accuracy for the dissociation energy is M05-2X with a relative error of only 1%, but the M06, M06-HF, and M06-2X functionals also did quite well with absolute errors of less than 10%. Every density functional tested except for MPWB1K and B3LYP yielded a more accurate dissociation energy than MP2 with the same basis set.

The fact that all of the new density functionals were able to qualitatively and quantitatively predict dissociation energies more accurately than the older functional B3LYP and even the wave function-based MP2 method, combined with the facts that most of the new functionals were able to produce good geometries for one of the conformers, that they did so at a relatively low computational cost, and that all of these functionals have already done relatively well for systems containing stronger hydrogen bonds and other types of noncovalent interactions, indicates that any one of these new density functionals would be an excellent candidate for modeling larger systems that contain hydrogen bonds of various strengths. The functional that showed the most versatility in this work and could therefore be awarded this study's "Best in Show" was the hybrid meta M06 functional, performing well both in its prediction of key geometric parameters and in the accuracy of its calculations of dissociation energies.

An area for further exploration of the versatility of these functionals would be to model the interaction of the sulfur lone pairs with various parts of the benzene molecule as Ringer et al. have done with wave function theory in a recent paper;[21] however, this is beyond the scope of the present study.

5. Summary

Four new density functionals, three slightly older functionals, and the popular B3LYP functional were tested for their abilities to predict the dissociation energies of three conformers of the H_2S−benzene dimer and to reproduce the key geometric parameters of the equilibrium conformation of this dimer. All of the functionals tested except B3LYP were able to correctly determine which of the three conformations of the dimer is the most stable. The functionals that are best able to reproduce the geometry of the equilibrium conformation of the dimer with a polarized triple-ζ basis set are M06-L, PWB6K, and MPWB1K, each having a mean unsigned relative error across the two experimentally verifiable geometric parameters of only 8%. The M05-2X functional yields the most accurate binding energy of a conformation of the dimer for which a binding energy calculated at the CCSD(T) level of theory is available; M05-2X predicts a binding energy only 0.02 kcal/mol different from that obtained by the CCSD(T) calculation. The M06 functional did well in both categories by yielding a good representation of the geometry of the equilibrium structure and by calculating a binding energy for a given conformation that is only 0.19 kcal/mol different from that calculated by CCSD(T).

Acknowledgment. This work was supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences.

References and Notes

(1) Rappé, A. K.; Bernstein, E. R. *J. Phys. Chem. A* **2000**, *104*, 6117.
(2) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2007**, *3*, 289.
(3) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.
(4) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
(5) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.
(6) Cramer, C. J. In *Essentials of Computational Chemistry. Theories and Models*; John Wiley and Sons: Chichester, U.K., 2004.
(7) Zhao, Y.; Tishchenko, O.; Truhlar, D. G. *J. Phys. Chem. B* **2005**, *109*, 19046.
(8) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2006**, *100*, 5121.
(9) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *213*, 364.
(10) Mignon, P.; Loverix, S.; Geerlings, P. *Chem. Phys. Lett.* **2005**, *401*, 40.
(11) Turki, N.; Milet, A.; Ouameralli, O.; Moszynski, R.; Kockanski, E. *THEOCHEM* **2002**, *577*, 239.
(12) Korth, H. G.; de Heer, M. I.; Mulder, P. *J. Phys. Chem. A* **2002**, *106*, 8779.
(13) Klein, R. A. *J. Comput. Chem.* **2003**, *24*, 1120.
(14) Ireta, J.; Neugebauer, J.; Scheffler, M. *J. Phys. Chem.* **2004**, *108*, 5692.
(15) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.*, in press.
(16) Wang, Y.; Paulus, B. *Chem. Phys. Lett.* **2007**, *441*, 187.
(17) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 6908.
(18) Perutz, M. F. *Philos. Trans. Phys. Sci. Eng.* **1993**, *345*, 105.
(19) Myers, J. K.; Pace, C. N. *Biophys. J.* **1996**, *71*, 2033.
(20) Tauer, T. P.; Derrick, M. E.; Sherrill, C. D. *J. Phys. Chem. A* **2005**, *109*, 191.
(21) Ringer, A. L.; Senenko, A.; Sherrill, C. D. *Protein Sci.* **2007**, *16*, 2216.
(22) Woon, D. E.; Dunning, T. H., Jr *J. Chem. Phys.* **1993**, *98*, 1358.
(23) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1995**, *96*, 6796.
(24) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley and Sons: New York, 1986.
(25) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 5656.
(26) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2006**, *110*, 13126.
(27) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101.
(28) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
(29) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 6624.
(30) Zhao, Y.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2701.
(31) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Phys.* **2005**, *123*, 161103.
(32) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 1009.

(33) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. C*, in press.

(34) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703.

(35) Frisch, M. J.; Trucks, G. W.; Schegel, H. B.; Robb, G. E. S. M. A.; Cheeseman, J. R.; Montgomery, J. A.,Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T. ; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M. P. M. W.; Gill; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian03*, Version c01; Gaussian, Inc.: Wallingford, CT, 2003.

(36) Zhao, Y.; Truhlar, D. G. *MN-GFM: Minnesota Gaussian Functional Module*, Version 3.0, University of Minnesota, Minneapolis, MN, 2007.

(37) Boys, S. F.; Bernardi, D. *Mol. Phys.* **1970**, *19*, 553.

(38) Arunan, E.; Emilsson, T.; Gutowsky, H. S.; Fraser, G. T.; Oliveira, G. D.; Dykstra, C. E. *J. Chem. Phys.* **2002**, *117*, 9766.

(39) Dobrowolski, J.; Jamróz, M. *J. Mol. Struct.* **1993**, *293*, 147.

(40) Gauss, J.; Stanton, J. F. *J. Phys. Chem. A* **2000**, *104*, 2865.

(41) Edwards, T. H.; Moncur, N. K.; Snyder, L. E. *J. Chem. Phys.* **1967**, *46*, 2139.

JP8018364