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Accurate DFT Descriptions for Weak Interactions of Molecules Containing Sulfur

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Abstract: Dispersion corrected atom centered potentials (DCACPs) have been shown to significantly improve the density functional theory (DFT) description of weak interactions. In this work, we have calibrated a DCACP for sulfur in combination with the widely used Generalized Gradient Approximation (GGA) BLYP, thereby augmenting the existing library of DCACPs for the first- and second-row elements H, C, N, O, and rare gases. Three weakly bound complexes as well as elemental (orthorhombic) sulfur are used as test cases to evaluate the transferability of the DCACP to different chemical environments. It is found that the sulfur DCACP systematically improves the agreement of DFT-calculated weak interactions with respect to MP2 and CCSD(T) level results.

I. Introduction

Dispersion corrected atom centered potentials (DCACPs) were introduced[1] to address the inadequate treatment of dispersion forces in Kohn−Sham density functional theory (DFT) when used in conjunction with approximated local or semilocal exchange-correlation functionals. The widely used generalized gradient approximation (GGA) and local density approximation (LDA) functionals are intrinsically unable to correctly reproduce dispersion forces, since dispersion forces are, by their nature, a nonlocal effect, whereas these functionals only depend on local quantities (density or density gradient). The procedure reported in the recent literature[1,2] constructs an analytic atom-centered correction term calibrated such that the treated DFT method correctly reproduces the MP2 or CCSD(T) level binding energy for a dispersion-dominated interaction. Existing work demonstrates that DCACPs can significantly improve the DFT description of dispersion interactions of rare gases (He, Ne, Ar, Kr) and molecules involving elements C, H, N, and O for a wide variety of chemical environments.[2−6] In a similar approach aimed at mixed quantum mechanical/molecular mechanical calculations, DiLabio[7] also makes use of adjustable atom centered potentials (termed Quantum Capping Potentials) of carbon atoms to successfully describe dispersion forces between hydrocarbon molecules in DFT calculations. A number of other methods to recover the dispersion forces in DFT exist; attempts have been made to directly include dispersion forces in the DFT formalism[8,9] promising a more rigorous treatment, but these approaches are currently too time-consuming for any practical applications or are otherwise limited. Other authors use a purely empirical van der Waals correction,[10] similar to the approach taken with DCACPs.

In this work, a DCACP was calibrated for sulfur using CCSD(T)/aug-cc-pVTZ calculations of the weakly interacting CS_2 dimer as a reference. The resulting DCACP is hypothesized to be generally valid for weak interactions arising from other chemical environments, i.e. to exhibit good transferability. To assess the transferability of the DCACP to chemical environments differing significantly from the calibration system, the DCACP was applied to four test systems (Figure 1): solid elemental sulfur; the SO_2 dimer; a hydrogen bonded $CH_3OH-S(CH_3)_2$ complex; and to the internal rotation of 2′,3′-dideoxytiazofurin. For all systems, results from DFT with DCACPs were compared to uncorrected DFT and to high-level benchmark (MP2 or CCSD(T)) calculations or experimental data. DFT results for the test systems are reported using the BLYP functional, which has been found previously to perform well in conjunction with DCACPs compared with other functionals (PBE, BP).[2] BLYP usually shows the most repulsive van der Waals interactions among GGA functionals, hence the DCACP for BLYP is

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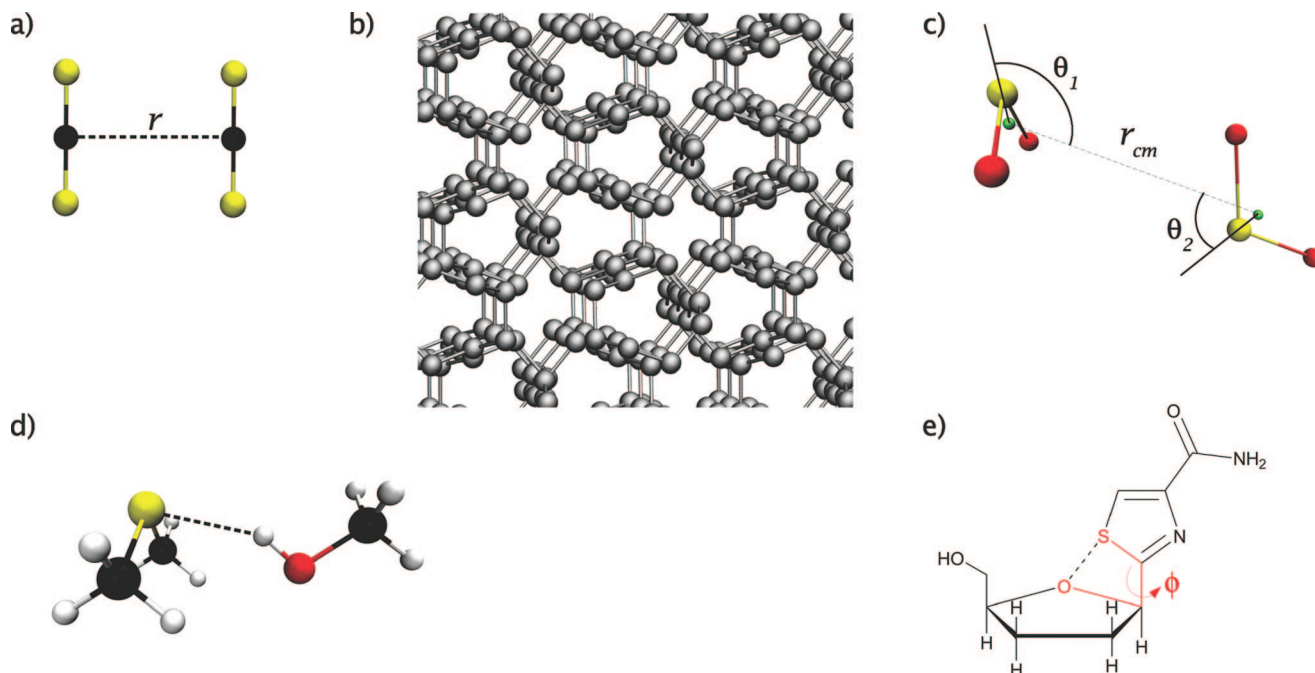ll Laboratory of Computational Chemistry and Biochemistry, Ecole Polytechnique Fédérale de Lausanne.

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Figure 1. Molecular structures of the systems that were assessed. (a) CS_2 dimer: all 6 atoms lie in one plane, the two linear CS_2 molecules are parallel. (b) Crystalline cyclic octasulfur: the unit cell (orthorhombic, $a = 10.38$ Å, $b = 12.75$ Å, $c = 24.41$ Å, space group no. 70, *Fddd*) contains 16 S_8 molecules. Experimentally determined structure.[20] (c) SO_2 dimer: C_s symmetry, r_{cm} is the distance between the centers of mass, θ_1 or θ_2 is the angle formed by the two centers of mass and the sulfur atom of the respective SO_2 molecule. (d) Methanol dimethylsulfide complex: C_s symmetry. (e) 2′,3′-Dideoxytiazofurin, experimentally determined crystal structure.[30]

consistently attractive[2] and therefore most likely to meaningfully represent dispersion forces.

II. Method

A. Construction, Calibration, and Testing of the DCACP for S. The dispersion correction consists of an atom-centered term which is applied to every atom in the system. The DCACP for sulfur has the mathematical form of the nonlocal f-channel of Goedecker type[11] pseudopotentials

$$v_{f,\mathbf{R_I}}^{\text{DCACP}}(\mathbf{r}, \mathbf{r}') = \sum_{m=-3}^{+3} Y_f^m(\hat{\mathbf{r}}) p_f(r; \sigma_2) \sigma_1 p_f(r'; \sigma_2) Y_f^{m*}(\hat{r}') \quad (1)$$

where $r = |\mathbf{r} - \mathbf{R_I}|$ is the distance from sulfur nucleus I, $\hat{\mathbf{r}}$ is the unit vector in the direction of $\mathbf{r} - \mathbf{R_I}$, and Y_f^m denotes spherical harmonics of angular momentum $l = 3$. Each atom at position $\mathbf{R_I}$ in the system adds a $v_{\mathbf{R_I}}^{\text{DCACP}}(\mathbf{r}, \mathbf{r}')$ term to the external potential $v_{\text{ext}}(\mathbf{r}, \mathbf{r}')$ of the system, such that the total external potential is $v'_{\text{ext}}(\mathbf{r}, \mathbf{r}') = v_{\text{ext}}(\mathbf{r}, \mathbf{r}') + \sum_I v_{\mathbf{R_I}}^{\text{DCACP}}(\mathbf{r}, \mathbf{r}')$. The DCACP for each atom is completely specified by two parameters that are determined by the calibration procedure: σ_1, which determines the amplitude of the potential, and σ_2, which describes the width of the radial projector operator p_f. These parameters must be calibrated specifically for each element and exchange-correlation functional. In this work, the DCACP parameters were determined for the GGA functional BLYP with respect to sulfur.

The calibration follows a recently established method[2] and proceeds by minimizing a penalty functional

$$\mathscr{P}(\sigma_1, \sigma_2) = |E_{\text{minpoint}}^{\text{Benchmark}} - E^{\text{DCACP}}(r_{\text{min}})|^2 + |E_{\text{midpoint}}^{\text{Benchmark}} - E^{\text{DCACP}}(r_{\text{mid}})|^2 + \sum_I w_I F_I^2 \quad (2)$$

where r_{min} and r_{mid} are the equilibrium and midpoint distance of the intermolecular interaction energy curves of the CS_2 dimer given by benchmark calculations; the midpoint is the distance where the interaction energy is half the equilibrium energy. F_I is the force on nucleus I of the complex at the benchmark equilibrium distance, r_{min}. The weighting factor w_I determines the relative importances of the ionic force term and energy terms in the penalty functional and has units of distance. It was chosen as $w_I = 100$ atomic units for all sulfur atoms and zero for the carbon atoms, analogous to previous calibrations of the other elements; details on the determination of the weighting factor can be found elsewhere.[2]

B. Computational Methods. The performances of the DFT and dispersion corrected-DFT methods were evaluated based on predictions for geometries and energies of weak interactions. Intermolecular dissociation energies were reported in terms of D_e in the notation of Herzberg,[12] i.e. zero point vibrational and thermal contributions were excluded. DFT energies were computed using the plane-wave code CPMD[13] with the pseudopotentials of either Goedecker et al.[11] (using a plane-wave cutoff of 170 Ry) or Troullier and Martins[14] (using a plane-wave cutoff of 70 Ry). The nuclear geometries for DFT calculations were fully relaxed using the same level of theory as the DFT computed energies, except where noted otherwise. Therefore, for most cases, the DFT energies were assessed using geometries that were different than the benchmark geometries. The ability to correctly predict theoretical or experimental benchmark geometries was itself part of the DFT performance evaluation. Benchmark geometries were taken either from theory or experiment, as explained in the Results. In cases where benchmark geometries were computed, we used MP2/aug-cc-

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pVTZ or higher wave function theory methods. Benchmark energies were computed at a level of wave function theory that was considered appropriate and reasonably computationally affordable for each case, ranging from MP2/aug-cc-pVDZ (for 2′,3′-dideoxytiazofurin) to CBS-QB3 (for the $CH_3OH-S(CH_3)_2$ complex). For example, a recent assessment found that MP2/6−31+G(d,p) and CCSD(T)/6−311+G(d,p) gave reasonable results for dispersion-dominated interactions, but a complete basis set extrapolation (CBS-QB3) was needed for accurate treatment of hydrogen bond energies.[15] All benchmark energies were computed using either the MOLPRO 2006.1[16] or Gaussian03[17] software packages.

III. Results

A. Calibration. Ideally, DCACPs are calibrated using molecular complexes which are (a) primarily bound by dispersion forces; (b) closed shell systems with a well defined ground state; and (c) small enough to be treated with high-level (MPn, CCSD(T)) methods. To develop a DCACP for sulfur, we chose the CS_2 dimer in its parallel conformation as a reference system (symmetry D_{2h}, Figure 1(a)). The parallel conformation cancels quadrupole moment electrostatic contributions to the intermolecular interaction. CS_2 is analogous to CO_2, which had previously been used to calibrate the DCACP for oxygen.[2] Compared to CO_2, CS_2 is highly polarizable and exhibits very weak electrostatic interactions with the environment.[18] This suggests that the CS_2 dimer will interact primarily via dispersion and exchange forces, making it an ideal candidate for calibration of the sulfur DCACP.

The benchmark method (CCSD(T)/aug-cc-pVTZ with counterpoise correction)[19] predicted a significant dispersion interaction for the CS_2 dimer. We found an interaction energy minimum of −5.9 kJ/mol at an intermolecular separation distance of $r = 4.10$ Å (Figure 2). In the range of $r = 3.5$ to 5.5 Å, the benchmark interaction energy was consistent with a fitted Lennard-Jones type 12−6 potential at the 1% significance level (χ^2 test). By comparison, BLYP predicted a purely repulsive interaction at all intermolecular distances.

The sulfur DCACP was calibrated using the existing carbon DCACP[2] for the two carbon atoms in the CS_2 dimer, and the sulfur DCACP parameters σ_1 and σ_2 were determined by minimizing the penalty functional given by eq 2. Table 1 shows the sulfur DCACP parameters found for the DFT functional, BLYP. When applied to a large range of CS_2 dimer intermolecular distances, the calibrated sulfur DCACP gave good agreement with the CCSD(T) benchmark (Figure 2).

B. Transferability. To evaluate the transferability of the sulfur DCACP to chemical environments other than that of the calibration system, four systems were evaluated (geometries shown in Figure 1). In all cases, calculations using the existing suite of DCACPs for H, C, N, and O,[2] together with the newly calibrated sulfur DCACP, were compared to both uncorrected DFT and high level benchmark calculations, where possible.

Crystalline Orthorhombic Sulfur. Crystalline orthorhombic sulfur (also known as cyclic octasulfur), having a unit cell that consists of 16 S_8 molecules, has been well characterized at a temperature of 100 K by X-ray diffraction.[20] In a simple qualitative assessment of DFT predictions for this crystal,
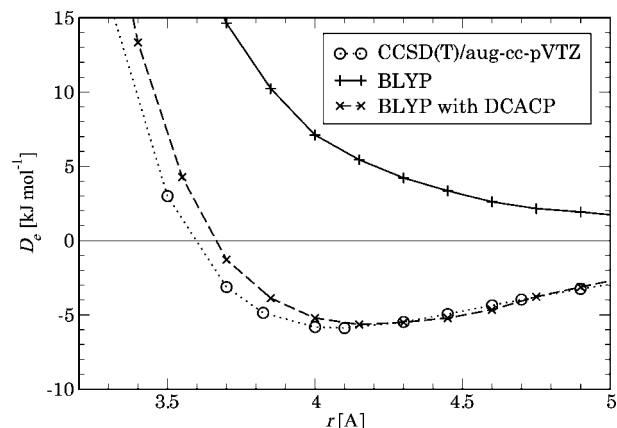

Figure 2. The calculated CS_2 dimer interaction energy versus intermolecular distance (r) using three methods. In all cases (BLYP, BLYP with DCACP, and CCSD(T)), the C−S bond lengths were kept fixed at 1.558 Å (based on a B3LYP/6−311+G(2d) geometry optimization of the monomer[34] and in agreement with the experimental value),[35] and r was the only internal coordinate varied. When BLYP is used with the calibrated DCACP, an interaction energy minimum of −5.6 kJ/mol is found at a separation distance of $r = 4.15$ Å, in agreement with the benchmark method (CCSD(T)/aug-cc-pVTZ with counterpoise correction).[19] By contrast, uncorrected BLYP predicts a purely repulsive interaction.

Table 1. Sulfur DCACP Calibration Results

functional	σ_1 [Hartree]	σ_2 [Bohr]	E_{min} [Hartree]	E_{mid} [Hartree]
BLYP	$-1.393 \cdot 10^{-3}$	3.273	$-2.242 \cdot 10^{-3}$	$-1.004 \cdot 10^{-3}$
benchmark[a]	-	-	$-2.244 \cdot 10^{-3}$	$-1.001 \cdot 10^{-3}$

[a] CCSD(T)/aug-cc-pVTZ with counterpoise correction.[19]

the DFT methods were used to fully relax the geometry of the crystal in orthorhombic periodic boundary conditions; the experimental crystal structure geometry was used as an initial guess, and the experimentally observed lattice parameters were imposed. At the relaxed geometry, the association energy of the crystal was determined, defined as the total energy of the crystal structure divided by 16, minus the energy of the S_8 monomer.[36] In this qualitative test, BLYP wrongly predicted a pure repulsive, positive association energy (87 kJ/mol), indicating that the crystal structure should not exist. By comparison, BLYP with the sulfur DCACP predicted a negative association energy (−82 kJ/mol), suggesting that crystal structure formation is favorable with respect to the gas phase S_8 monomer.

In a more sophisticated test, the crystal structure lattice vector lengths a, b, c were allowed to vary isotropically (with the lattice angles kept fixed). At each lattice volume, the crystal structure geometry was completely relaxed, with the aim of finding the lattice volume that would correspond to a global energy minimum.[37] Within a computationally feasible interval around the experimental value (Figure 3), BLYP never predicted a favorable association energy. By contrast, BLYP with sulfur DCACP found a minimum of the association energy with lattice vectors that are only 3.4% longer than the experimentally observed lengths. In summary, conventional BLYP does not even qualitatively correctly predict the existence of orthorhombic elemental sulfur. However, when
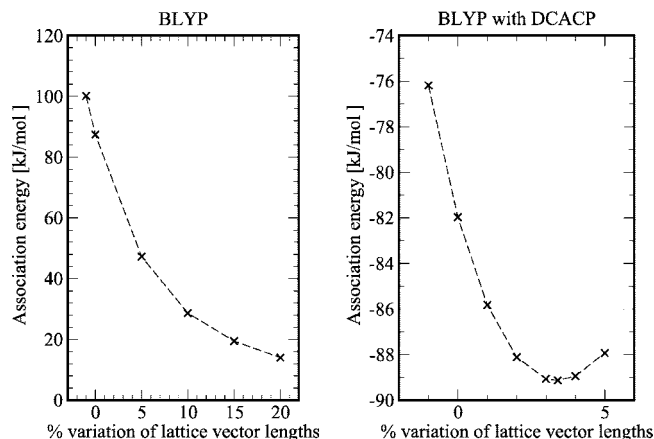
Figure 3. The crystal association energy was evaluated at several different cell parameters for orthorhombic sulfur, using both conventional BYLP (left) and BLYP with DCACP (right). The crystal geometry was fully relaxed at each cell size. The horizontal axis shows the amount by which the cell parameters *a*, *b*, *c* were isotropically varied from the experimentally observed lengths. The suggested energetic minimum for BLYP with DCACP, at lattice length variation of 3.4%, was interpolated from the other points.

the sulfur DCACP is applied, BLYP predicts favorable crystal structure formation, having an energetic minimum at lattice vectors that are close to those observed experimentally.

To further evaluate the sulfur crystal calculations, we compared predicted and experimental enthalpy of deposition (i.e., the negative of the enthalpy of sublimation) at 0 K. The computed deposition enthalpy was given by the calculated association energy of the relaxed structure at the optimized crystal lattice lengths (−89.1 kJ/mol), plus the estimated change in zero point energy (ZPE) in going from the gas phase to solid phase (−0.3 kJ/mol).[38] We obtain a value of −89.4 kJ/mol, which can be interpreted as the energy of forming orthorhombic sulfur from gaseous S_8 at a temperature of 0 K. By comparison, the experimental deposition enthalpy, extrapolated to 0 K, is −105.7 kJ/mol.[39] This shows that the DCACP correction not only corrects the qualitative DFT prediction of a stable crystal structure but also estimates the quantitative stability of the crystal with reasonable accuracy.

The SO₂ Dimer. The SO_2 interaction is important in atmospheric chemistry, where the photooxidation of 2 SO_2 to SO_3 + SO is believed to proceed mainly via a weakly bound gas phase SO_2 dimer.[23] Based on the theoretical and experimental data by Bone et al.,[24] the minimum energy configuration of the SO_2 dimer has C_s symmetry, as shown in Figure 1(c). In this conformation, BLYP incorrectly predicted a very weak binding energy of only −2.2 kJ/mol (Table 2). By contrast, BLYP with DCACPs predicted a −11.2 kJ/mol interaction energy, in close agreement with the benchmark result of −11.5 kJ/mol (CCSD(T)/aug-cc-pVTZ with counterpoise correction).[19] Notably, BLYP with sulfur and oxygen DCACPs predicted significantly stronger SO_2 dimer binding energy than BLYP with the DCACP corrections for oxygen only. Both electrostatics and dispersion forces control the interaction between SO_2 molecules, which are strongly polar (SO_2 experimental dipole moment = 1.633 Debye, i.e. comparable to that of water). Hence, although the sulfur DCACP was calibrated using a dispersion-dominated system (the CS_2 dimer), its applicability extends to this system, where electrostatics are also important.

Table 2. Binding Energies of the SO₂ Dimer[a]

method	D_e [kJ/mol]	r_{cm} [Å]	θ_1	θ_2
benchmark[b]	−11.5	3.78	119.5	58.0
BLYP	−2.2	4.00	132	64
BLYP with oxygen DCACP only	−6.2	3.94	130	68
BLYP with oxygen and sulfur DCACPs	−11.2	3.93	133	65
experimental[32]	N/A	3.822(1)	127.0(20)	60.5(6)

[a] DFT geometries were fully optimized at the indicated levels. See Figure 1(c) for the meaning of geometrical parameters r_{cm}, θ_1, and θ_2. [b] MP4(SDQ)/aug-cc-pVTZ geometry and CCSD(T)/aug-cc-pVTZ energy with counterpoise correction.[19]

Table 3. Hydrogen Bond Binding Energies and Equilibrium Geometry Parameters of the CH₃OH−S(CH₃)₂ Complex[a]

method	D_e [kJ/mol]	S···H distance [Å]
benchmark[b]	−22.6	2.33
BLYP	−14.3	2.44
BLYP with DCACPs for C, H, O	−24.0	2.35
BLYP with DCACPs for C, H, O, S	−26.2	2.33

[a] DFT geometries were fully optimized at the indicated levels. [b] MP2/aug-cc-pVTZ geometry and CBS-QB3 energy[33] evaluated at the MP2 geometry.

The Hydrogen Bonded CH₃OH−S(CH₃)₂ Complex. Hydrogen bonding to sulfur may be relevant in biological systems, where ligands could interact with methionine or cysteine groups, hence modeling efforts may require accurate treatment of this contact. BLYP significantly underestimated the hydrogen-bond binding energy (−14.3 kJ/mol) and overestimated the hydrogen-bond distance (2.44 Å), when compared to the CBS-QB3 benchmark energy and MP2/aug-cc-pVTZ geometry (−25.3 kJ/mol and 2.33 Å; Table 3). By comparison, BLYP with DCACPs improved both the equilibrium distance (2.33 Å) and binding energy (−26.2 kJ/mol) of the CH₃OH−S(CH₃)₂ hydrogen bond. The sulfur DCACP makes a small but significant contribution (ca. 2 kJ/mol) to the total binding energy, in comparison to the other DCACPs. It is worth noting that dispersion forces may contribute significantly to hydrogen bonding,[25−27] which may partly explain why BLYP sometimes poorly estimates this interaction.[28]

The Intramolecular Rotation of 2′,3′-Dideoxytiazofurin. The molecule 2′,3′-dideoxytiazofurin [2-(2′,3′-dideoxy-β-D-glycero-pentafuranosyl)thiazole-4-carboxamide, Figure 1] is a biologically active compound which has been shown to have clinically effective antitumor activity.[29] The molecule features an unusually close distance (2.83 Å) between the sulfur atom in the thiazole ring and the oxygen atom O1′ in the furanose ring in its crystal structure;[30] several thiazole nucleoside analogs exhibit the same close contact in their crystal structures,[31] which suggests that it is not due to a crystal packing effect but to an attracting force between these two atoms. This attraction was quantified by calculating the total energy at varying O−C−C−S dihedral angles, ϕ (Figure 1). Figure 4 shows the variation of the total energy as a function of ϕ. BLYP predicted correctly the qualitative behavior of the energy profile but was systematically biased low by 2−3 kJ/mol. This reflects the strong electrostatic component of the S−O interaction that is usually reasonably accounted for by GGAs. By comparison, BLYP with DCACPs exhibited very good agreement with the benchmark data, having a root mean squared error of 0.73 kJ/mol with respect to benchmark results (MP2/aug-cc-pVDZ counterpoise
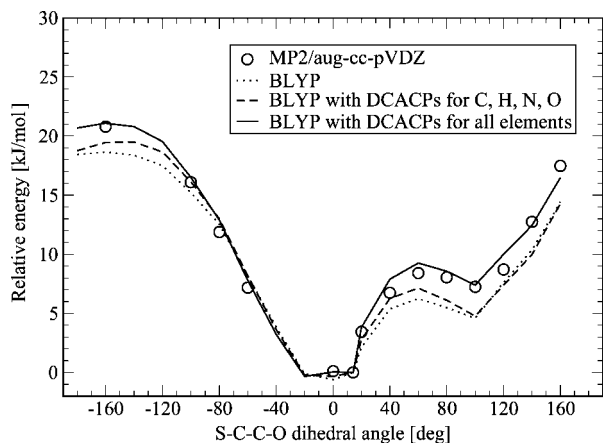
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Figure 4. The relative energy of 2′,3′-dideoxytiazofurin as a function of the S−C−C−O dihedral angle. For each level of theory, the zero of the energy scale is set to the calculated total energy for the experimentally observed crystal geometry (S−C−C−O dihedral angle of 14.1). In the remaining calculations, only the S−C−C−O dihedral angle was varied, while the other internal coordinates were kept fixed.

correction).[19] Additional computations using only DCACPs for the elements C, N, O, and H showed that the marginal contribution of the sulfur DCACP is significant, relative to the other DCACPs (Figure 4).

IV. Conclusion

The library of dispersion corrected atom centered potentials for the GGA functional BLYP[2] has been augmented by a third-row element, sulfur. The very good results from four simple sulfur-containing test systems show that the sulfur DCACP is highly transferable to chemical environments other than the calibration system. These tests show that, although the DCACP was calibrated in a simple, almost purely dispersion controlled system (the CS_2 dimer), significant improvements to the calculation of binding energies are also achieved in weakly bound systems having strong electrostatic interactions. Moreover, our results demonstrate that, in several chemical environments, the sulfur DCACP makes an important contribution to the weak interaction beyond that of the DCACPs for other elements. With the sulfur atom DCACP now at hand, there is now a full set of DCACPs available for modeling a standard protein in DFT. A library of DCACPs applicable to BLYP, PBE, and BP for sulfur and other elements is available online at our Web site [see http://lcbcpc21.epfl.ch/dcacp/dcacp.html].

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(36) Association energies are reported based on a fixed plane wave energy cutoff of 70 Ry. Additional computations demonstrated that basis set convergence was achieved to within <1 kJ/mol at this energy cutoff. To avoid the introduction of plane wave artifacts, the gas phase S_8 monomer was computed using the same energy cutoff, boundary conditions (orthorhombic, periodic), and unit cell dimensions as the crystal. Additional computations demonstrated that at these specifications, the monomer has negligible self-interaction across the periodic cell boundary; variation of the unit cell dimensions for the monomer contributed negligibly (<0.1 kJ/mol) to the association energy.

(37) Association energies are reported based on a plane wave energy cutoff of 70 Ry. Additional computations demonstrated that basis set convergence was achieved to within <1 kJ/mol at both the largest and smallest lattice parameters applied.

(38) The change in ZPE upon deposition at 0 K was estimated from the computed ZPE of sulfur solid (32.1 kJ/mol) by Delley[21] minus the ZPE value of gas phase S_8 (32.4 kJ/mol) calculated from the measured vibrational frequencies of S_8 reported in NIST-JANAF thermochemical tables.[22]

(39) The deposition enthalpy of S_8 at 0 K was estimated as follows: $\Delta H^\circ_{\text{deposition,0K}} = H^\circ(\text{crystal, 0 K}) - H^\circ(\text{crystal, 298.15 K}) + H^\circ(\text{crystal, 298.15 K}) - H^\circ(\text{gas, 298.15 K}) + H^\circ(\text{gas, 298.15 K}) - H^\circ(\text{gas, 0 K})$. The difference terms $H^\circ(\text{crystal, 0 K}) - H^\circ(\text{crystal, 298.15 K})$ and $H^\circ(\text{gas, 298.15 K}) - H^\circ(\text{gas, 0 K})$ were directly taken from reference thermochemical tables,[22] and the difference term $H^\circ(\text{crystal, 298.15 K}) - H^\circ(\text{gas, 298.15 K})$ is given by the experimental negative of the enthalpy of sublimation taken from the same reference tables.[22]