Accurate Modeling of Organic Molecular Crystals by Dispersion-Corrected Density Functional Tight Binding (DFTB)

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S *Supporting Information*

ABSTRACT: The ambitious goal of organic crystal structure prediction challenges theoretical methods regarding their accuracy and efficiency. Dispersion-corrected density functional theory (DFT-D) in principle is applicable, but the computational demands, for example, to compute a huge number of polymorphs, are too high. Here, we demonstrate that this task can be carried out by a dispersion-corrected density functional tight binding (DFTB) method. The semiempirical Hamiltonian with the D3 correction can accurately and efficiently model both solid- and gas-phase inter- and intramolecular interactions at a speed up of 2 orders of magnitude compared to DFT-D. The mean absolute deviations for interaction (lattice) energies for various databases are typically 2–3 kcal/mol (10–20%), that is, only about two times larger than those for DFT-D. For zero-point phonon energies, small deviations of <0.5 kcal/mol compared to DFT-D are obtained.

SECTION: Molecular Structure, Quantum Chemistry, and General Theory
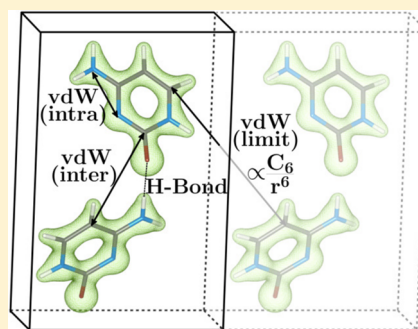
Accurate and efficient modeling of inter- and intramolecular interactions both in the gas and solid phase of organic molecules is mandatory for a variety of applications and represents a very active research field.[1−7] The theoretical description of gas-phase dimers, supramolecular host−guest complexes, and organic crystals mainly relies on the correct description of noncovalent interactions. Crucial parts of these intermolecular forces are the hydrogen bonding and van der Waals (vdW) interactions.[8] In principle, high-level quantum chemical methods can seamlessly describe all of the local and nonlocal interactions but are computationally too demanding for large complexes and especially for molecular crystals of larger molecules. Empirical potentials (force fields) and London dispersion-corrected density functional theory (DFT-D) are the mainly used alternatives.[9] Recent developments and applications of different DFT-D methods demonstrated their predictive power in both molecular complexes and organic solids.[10,11] For example, our well-established semiclassical DFT-D3 scheme successfully participated recently in the SAMPL4 blind test for prediction of host−guest association free energies.[12] It was further shown that semilocal density functionals in a huge plane wave basis augmented with the D3 London dispersion correction can calculate sublimation energies with an accuracy of 1 kcal/mol.[3,13] Similarly accurate results are obtained with the Tkachenko−Scheffler (TS) many-body dispersion correction (MBD)[14,15] and E. Johnson's exchange dipole model (XDM).[16] G. Beran proposed a fragment-based hybrid many-body interaction model, which is also capable of calculating lattice energies with chemical accuracy.[2,17] These methods have already been used in the field of crystal structure prediction.[18]

Though having a good accuracy−cost ratio, the DFT-D methods cannot be applied to thousands of large complexes or organic crystals in a reasonable time. Especially for prescreening of multiple conformations in organic crystal structure prediction (or likewise in crystal structure refinement), faster methods are required. Purely empirical force fields are typically not accurate enough for a reasonable energy ranking of low-lying structures, which results in a large number of cases that have to be treated by DFT.[19] This obvious gap between force fields and DFT could be covered by semiempirical methods as sketched in Figure 1. In this context, we recently reduced the computational cost of DFT calculations by applying a small atomic orbital basis set (of mainly double-ζ quality) and correcting the arising basis set superposition error (BSSE) by a semiempirical pair potential gCP.[20] For plain Hartree−Fock in a nearly minimal basis set, we additionally corrected empirically for the basis incompleteness and compiled the HF-3c method.[21] Both approaches were successfully tested on organic crystals as well.[3,22]

Here, we investigate the performance of the density functional tight binding (DFTB) method DFTB3 for binding (interaction) energies of small to large molecular gas-phase complexes (6−177 atoms) and organic molecular crystals. This method is based on a third-order expansion of the Kohn−Sham total energy with respect to charge density fluctuations. The arising matrix elements are modified by a self-consistent charge (SCC) redistribution. The modification corresponds to an on-
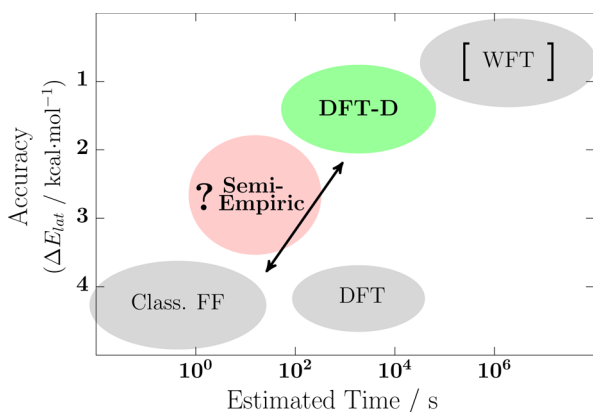
Figure 1. A schematic view of the accuracy–computational cost ratio for different methods is given. The accuracy is exemplarily given for the calculation of organic crystal lattice energies. Wave function theory methods (WFT) are expected to give the correct result in principle but cannot be applied routinely. The gap between force fields and DFT-D is highlighted.

site repulsion for short distances and to a Coulomb interaction at long distances with the correct Coulomb limit. In the latest version, an additional damping of the pair interactions involving hydrogen atoms is included. This significantly improves the description of hydrogen-bonded systems and proton trans-fer.[23−26] We abbreviate this SCC-DFTB3 method as DFTB throughout the Letter. This model Hamiltonian must be additionally corrected to account for nonlocal electron correlation effects, with the London dispersion interaction as the most dominant contribution. Because the charge density of the DFTB method is (mainly due to its minimal basis) not very accurate, it is ideal to use a correction scheme that does not explicitly depend on the electronic structure, and hence such an augmentation in the TB context has been proposed already some time ago.[27]

The atom-pairwise D3 correction solely uses the geometry information to calculate the dispersion energy

$$E_{\text{disp}} = -\frac{1}{2} \sum_{n=6,8} \sum_{i,j}^{N} s_n \frac{C_n^{ij}}{\| \mathbf{r}_{ij} \|^n + f(R_0^{ij})^n} \tag{1}$$

where $C_{6/8}^{ij}$ are the leading order dipole–dipole and dipole–quadrupole dispersion coefficients and r_{ij} is the distance between the atom pairs i,j.[28] The s_6 scaling coefficient is set to unity to ensure the correct long-range behavior. The Becke–Johnson[29] rational damping function $f(R_0^{ij})$ is used to match the long- and medium-range dispersion contribution from D3 with the semilocal correlation captured by DFTB.[30] The C_6 dispersion coefficients depend geometrically on the molecular environment and are precalculated by time-dependent DFT and utilizing the Casimir–Polder relation.[31,32] Because of its small numerical complexity, the D3 correction is ideally suited for a coupling with inherently fast electronic structure methods where more complicated density-based schemes (e.g., refs 33 and 34) would lead to a huge computational overhead.

In the following, two standard benchmark sets are investigated. The molecular S66[35] set consists of 66 small- to medium-sized dimers in their equilibrium geometry. It contains purely vdW-bonded, purely hydrogen-bonded, and mixed systems. In the S66 × 8 set, the S66 dimers are considered at eight different center of mass distances. This set is the defacto standard for testing noncovalent interactions in gas-phase

dimers. The reference values are basis set extrapolated CCSD(T) energies. Because similar high-level calculations are not affordable for molecular crystals, reliable reference energies can only be extracted from experiment. E. Johnson compiled a test set of molecular crystals, which was extended and refined by A. Tkatchenko.[14−16] Similar to the S66 set, these X23 systems consist of purely vdW-bonded, purely hydrogen-bonded, and mixed systems. The experimental sublimation energies are explicitly back-corrected to electronic lattice energies. In this way, one can directly compare the electronic energies with the provided reference data in full analogy to S66. Table 1 shows the mean absolute deviation (MAD) and mean

Table 1. MAD and MD of the Dissociation and Lattice Energies for the S66 × 8 and the X23 Test Set[a]

method	S66 × 8		X23	
	MAD	MD	MAD	MD
All Systems				
DFTB	2.17	−2.17	12.29	−12.29
DFTB-D3	0.79	−0.42	2.48	−0.22
PBE-D3[b]	0.35	0.24	1.07	0.43
PM7[c]	0.73	−0.13		
vdW-Bonded				
DFTB	2.22	−2.22	14.31	−14.31
DFTB-D3	0.54	0.37	1.80	0.23
PBE-D3	0.27	0.01	0.86	0.06
H-Bonded				
DFTB	2.36	−2.36	7.62	−7.62
DFTB-D3	1.30	−1.29	2.56	1.63
PBE-D3	0.55	0.55	1.27	1.21
Mixed				
DFTB	1.88	−1.88	16.06	−16.06
DFTB-D3	0.49	−0.35	4.19	−2.64
PBE-D3	0.20	0.14	1.50	0.13

[a]Data are given for uncorrected as well as dispersion-corrected (suffix D3) methods. All values are in kcal/mol, and a positive MD denotes an average overbinding. [b]PBE in a huge almost complete basis set according to refs 3 and 36. [c]PM7[37] is currently not applicable to crystals.
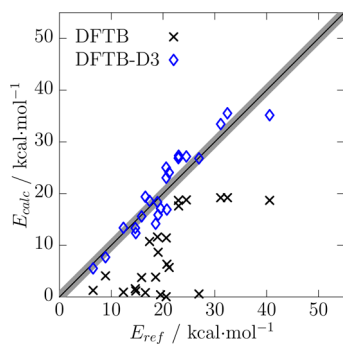
deviation (MD) of DFTB for both test sets. To put these values into perspective, DFT (PBE) as well as semiempirical PM7[37] values are included. The individual values are given in the Supporting Information (SI). The statistical data are separated in the different bonding situations to identify the main error sources. When judging the results, one should keep in mind that the mean S66 × 8 dissociation energy and the mean X23 lattice energy are 4 kcal/mol (range from 0.0 to 19.5 kcal/mol) and 20 kcal/mol (range from 6.5 to 40.6 kcal/mol), respectively.

The uncorrected DFTB significantly underestimates the binding in the S66 × 8 dimers by more than 54%. The MAD is approximately 2 kcal/mol for all binding motives. This (unsurprising) finding indicates that an important contribution is missing in the model Hamiltonian. The dispersion correction D3 reduces the mean error drastically with a residual MAD below 1 kcal/mol. The comparison of the hydrogen-bonded with the vdW-bonded systems shows that the main error originates in a partially wrong description of the delicate electrostatic and induction contributions in hydrogen bonds. The MAD for the vdW systems of about 0.5 kcal/mol is considered as very accurate and competitive to standard DFT.

To cross-validate this result, we additionally employ the benchmark sets S22 (small gas-phase dimers[38]), X40 (halogenated gas-phase dimers[39]), L7 (large gas-phase dimers and trimers[40]) with new DLPNO-CCSD(T)/ΔCBS/CP references (unpublished results), and S12L (large host–guest complexes[41]). The small DFTB-D3 MADs for these sets of 0.95, 1.66, 1.74, and 5.90 kcal/mol confirm the picture drawn above. This also indicates that the S66 × 8 test set seems to be representative for a large number of systems.[36] Though the results are worse than those for standard density functionals (the MAD on the PBE-D3/large basis set level is 0.35 kcal/mol[36] for S66 × 8), it is an improvement over other semiempirical methods if larger systems are considered. While PM7[37] has a slightly smaller MAD on the S66 × 8 set, it performs worse for the larger systems with MADs of 0.77, 1.69, 7.61, and 17.51 kcal/mol for the S22, X40, L7, and S12L benchmark sets. Due to the large errors for larger complexes (i.e., L7 and S12L), one cannot expect good PM7 results for organic crystals. The semiempirical PM6-DH2[42,43] performs slightly better than PM7. However, the larger deviations for L7 and S12L systems persist.

A similar picture of performance is observed for the lattice energies of the molecular crystals in X23. Periodic systems are most sensitive to the correct treatment of long-range interactions. The underbinding tendency of DFTB is more pronounced for X23 than that for S66, and its MAD is more than 60% of the mean lattice energy. The errors for the X23 lattice energies drop significantly to a small MAD of 2.5 kcal/mol on the DFTB-D3 level, which corresponds to only 12% of the mean lattice energy. Note that the dispersion-corrected DFTB-D3 is used without any electronic reparametrization, which demonstrates the robustness of the method.
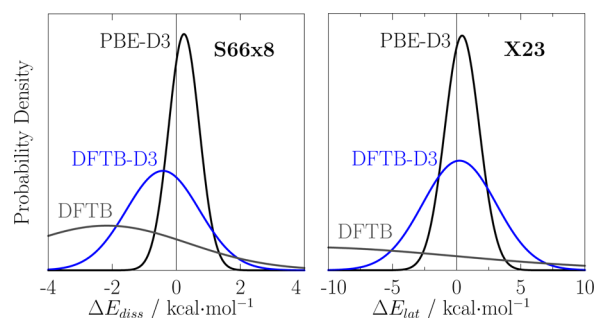
Figure 2 shows the individual values compared to the reference energies. The error of the back-corrected reference

Figure 3. Normal error distributions for the benchmark sets S66 × 8 and X23. The newly evaluated method DFTB-D3 is highlighted.

Figure 2. Correlation between the calculated DFTB and DFTB-D3 lattice energies with the experimental reference values. The gray shading denotes the uncertainty of the references of approximately 1.2 kcal/mol.[3]

energies is estimated to be 1.2 kcal/mol.[3] The linear correlation coefficient is 0.68 and 0.94 for DFTB and DFTB-D3, respectively. Similar to the molecular case, the MAD of the purely vdW-bonded systems is lower by 1.8 kcal/mol, that is, systems containing more complicated electrostatics (hydrogen- and mixed bonding motifs) are described slightly worse. A comparison between the performance for the gas-phase (S66 × 8) and the solid-phase (X23) test sets is sketched in Figure 3.

Aside from prescreening and electronic structure calculations of huge systems, DFTB-D3 can also be used as a cheaper alternative for derivative calculations. These are needed for

instance to explicitly calculate the phonon spectrum and to correct the electronic energies to enthalpies or free energies at finite temperatures. We computed the vibrational contribution to the X23 sublimation energies in the harmonic approximation (unscaled frequencies) and compare the resulting energy corrections with the recently published PBE-TS values.[15] The MAD between the two data sets is only 0.5 kcal/mol, which is comparable to the results known from molecular complexes.[41] For the calculation of the sublimation energy of a given crystal structure, we propose the following procedure. First, optimize the entire crystal structure including cell parameters at the general gradient approximated DFT level PBE-D3 in a large projector-augmented plane wave (PAW) basis. Then, calculate a single-point energy at the higher hybrid functional level PBE0-D3 at the PBE-D3 structure. Finally, correct for vibrational contributions using DFTB-D3 frequencies. For example, the frequency calculation of a cytosine crystal (in a supercell with 156 atoms) takes less than 1 h on a standard workstation with the `dftb+` and `dftd3` codes. In the DFT single-point calculation, other functionals (e.g., BLYP, TPSS, HSE06) or other London dispersion corrections (e.g., TS, MBD, XDM) could be used for comparison.

In this work, we have augmented an existing DFTB Hamiltonian (including full third-order correction, SCCs, and special hydrogen bond damping) with the latest first-principles London dispersion correction D3. The DFTB-D3 method was evaluated for both mostly organic gas-phase as well as solid structures with very promising results. The MAD of 2.5 kcal/mol obtained for the X23 lattice energies is exceptionally small for a semiempirical method. The analysis of different subsets in the benchmarks illustrated that the main error source for the DFTB-D3 method are the hydrogen-bonded systems. Although their description has improved in going from DFTB1 to DFTB3, this point clearly needs further improvements. The potential of the combined DFTB-D3 approach for organic crystal structure prediction and refinement was demonstrated on the X23 test set. Furthermore, the vibrational corrections on the DFTB-D3 level were compared to those obtained at the dispersion-corrected DFT level and showed good mutual agreement. In summary, the future for electronic-structure-based organic crystal structure prediction is bright when a kind of multilevel approach is employed.

■ COMPUTATIONAL METHODS

We utilized the DFTB Hamiltonian with full third-order correction and SCCs. The SCC tolerance is 10^{-7} au. We used the most recent Slater–Koster files provided by the group of M. Elstner. The hydrogen-containing pair potentials were addi-

tionally damped with an exponent of 4.2, which is the recommended value for proton transfers.[23,25,26] The Brillouin zone was sampled with a Γ-centered grid with at least 0.05 Å^{-1} k-points, generated via the Monkhorst–Pack scheme.[44] The London dispersion correction D3 was used in the Becke–Johnson damping variant with parameters $s_8 = 0.5883$, $a_1 = 0.5719$, and $a_2 = 3.6017$. The parameters were fitted on the S66 reference energies similar to the procedure in the original publication.[28] A similar DFTB-D3 parametrization was already tested on the S12L set and for calculations of electron impact mass spectra.[11,45] The X23 geometries were optimized on the DFTB-D3 level with a fixed unit cell with the approximate normal coordinate rational function optimizer ANCOPT[46,47] until the atomic forces were below 10^{-4} au. For all other benchmarks, the standard single-point energy approach was applied. Phonon frequencies were calculated at the Γ-point in a supercell approach. The vibrational corrections to the lattice enthalpy were calculated in the harmonic approximation similar to the reference approach.[15] In the X40 test set, systems including Br or I were excluded, and the Fe-containing complex in the S12L set was also disregarded due to missing Slater–Koster files.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A table of calculated lattice energies, experimental sublimation enthalpies, and vibrational contributions along with a computational methodology and DFTB-D3 optimized geometries for the X23 systems and the binding energies for the S66 database and detailed statistics for the S66 × 8, S22, X40, L7, and S12L sets. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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