

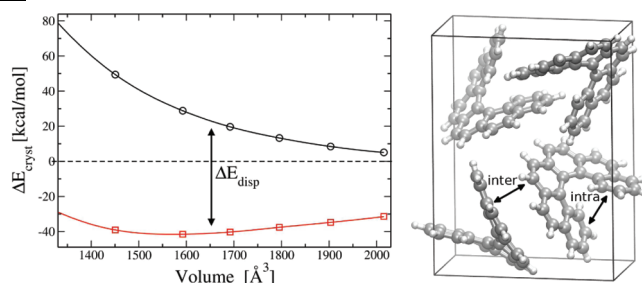
Dispersion-Corrected Density Functional Theory for Aromatic Interactions in Complex Systems

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CONSPECTUS



Aromatic interactions play a key role in many chemical and biological systems. However, even if very simple models are chosen, the systems of interest are often too large to be handled with standard wave function theory (WFT). Although density functional theory (DFT) can easily treat systems of more than 200 atoms, standard semilocal (hybrid) density functional approximations fail to describe the London dispersion energy, a factor that is essential for accurate predictions of inter- and intramolecular noncovalent interactions. Therefore dispersion-corrected DFT provides a unique tool for the investigation and analysis of a wide range of complex aromatic systems.

In this Account, we start with an analysis of the noncovalent interactions in simple model dimers of hexafluorobenzene (HFB) and benzene, with a focus on electrostatic and dispersion interactions. The minima for the parallel-displaced dimers of HFB/HFB and HFB/benzene can only be explained when taking into account all contributions to the interaction energy and not by electrostatics alone. By comparison of saturated and aromatic model complexes, we show that increased dispersion coefficients for sp^2 -hybridized carbon atoms play a major role in aromatic stacking.

Modern dispersion-corrected DFT yields accurate results (about 5–10% error for the dimerization energy) for the relatively large porphyrin and coronene dimers, systems for which WFT can provide accurate reference data only with huge computational effort. In this example, it is also demonstrated that new nonlocal, density-dependent dispersion corrections and atom pairwise schemes mutually agree with each other.

The dispersion energy is also important for the complex inter- and intramolecular interactions that arise in the molecular crystals of aromatic molecules. In studies of hexahelicene, dispersion-corrected DFT yields “the right answer for the right reason”. By comparison, standard DFT calculations reproduce intramolecular distances quite accurately in single-molecule calculations while inter- and intramolecular distances become too large when dispersion-uncorrected solid-state calculations are carried out. Dispersion-corrected DFT can fix this problem, and these results are in excellent agreement with experimental structure and energetic (sublimation) data. Uncorrected treatments do not even yield a bound crystal state.

Finally, we present calculations for the formation of a cationic, quadruply charged dimer of a porphyrin derivative, a case where dispersion is required in order to overcome strong electrostatic repulsion. A combination of dispersion-corrected DFT with an adequate continuum solvation model can accurately reproduce experimental free association enthalpies in solution. As in the previous examples, consideration of the electrostatic interactions alone does not provide a qualitatively or quantitatively correct picture of the interactions of this complex.

1. Introduction

Noncovalent interactions have been an active field of research in theoretical chemistry in the past years. Because

such interactions are inarguably of great importance in condensed matter physics, chemistry, and biology,^{1–3} the need for efficient and accurate methods to treat them is

obvious. While it is possible to describe small systems with highly accurate WFT (e.g., CCSD(T) at the estimated complete basis set (CBS) limit^{4,5}), the only routinely applicable wave function method for larger noncovalently bound systems is second-order perturbation theory (MP2⁶). However, MP2 performs poorly for aromatic interactions (of π - π stacking type in particular^{5,7,8}), converges slowly with respect to the quality of the one-particle basis set, and still displays a steep scaling behavior with system size (of order N^5 where N is the number of electrons).

On the other hand, while standard Kohn–Sham density functional theory (DFT) can easily handle large systems, it fails to correctly describe noncovalent interactions (NCI) in general. This in particular holds for the London dispersion interaction with its characteristic asymptotic R^{-6} decay behavior (R being some intermolecular distance), which is difficult to describe by local functionals of the exponentially decaying electron density (for early observations of this failure, see refs 9 and 10). However, the account of London dispersion is crucial to describe inter- and intramolecular NCI correctly. Therefore, the last years have seen an increased interest in the development of dispersion-corrected density functionals, which couple the computational efficiency of DFT with an improved description of NCI (e.g., see refs 11–17).

While the large amount of available benchmark NCI data^{18–20} has led to good insights into the behavior and accuracy of the mentioned methods for small- to medium-sized systems, much less is known for larger systems. Moreover, in many (bio)chemical systems localized charges are present, leading to a subtle interplay between London dispersion and Coulomb interactions, which complicates the so-called π - π stacking of aromatic molecules (for a recent example, see ref 21). A survey of aromatic NCI in typical supramolecular complexes reveals that charges in the complexes are more the rule than an exception.^{22,23} The topic of charged aromatic NCI also involves very important solvent–solute interactions, which must be considered when comparisons to experimental condensed phase data are made.

The quite mysterious flavor that encloses the term aromatic π - π stacking in the literature was the subject of a recent theoretical study.⁸ The role of the substituents in aromatic stacking was also clarified theoretically (for a recent review, see ref 24). According to modern understanding, special, nonlocal electron correlations between the π -electrons in the two interacting aromatic systems at small interplane distances do exist but are not much more pronounced

than in saturated hydrocarbons of similar size for systems with about 10 carbon atoms. There is also an indirect influence of the π -system through the special shape of the π -stacked complexes that allows a closer contact of the monomers (i.e., maximizing the attractive dispersion component) without concomitantly too much Pauli-exchange repulsion. For geometrical reasons, this is not possible in nonstacked or saturated molecules. There is also an important effect of the larger dispersion coefficients of sp^2 vs sp^3 hybridized carbon atoms, which is discussed below.

In this Account, we will try to show that modern dispersion-corrected DFT is able to correctly describe various types of aromatic interactions. Not only the common intermolecular situation but in addition the interplay between intra- and intermolecular NCI in a molecular crystal will be considered. We first shed some light on the relation between electrostatic and dispersion interactions in model complexes. Color coded plots of the electrostatic potential (ESP) are often used in the contemporary literature to rationalize aromatic NCI,²⁵ which is, as we will show, an oversimplification of the bonding. Before we discuss the four chemical examples, a brief outline of the quantum chemical procedures is given.

2. Quantum Chemical Methodology

Some of the systems studied in this Account are rather large for a quantum mechanical treatment, and the possible errors that arise from methodological and numerical approximations necessary to treat such systems should be discussed. Regarding DFT, from the numerical issues in the RI integral approximation, quadrature grid, and AO basis set, only the last point is relevant on a chemical precision scale. A triple- ζ basis set is often sufficient for structure optimization but yields basis set superposition errors (BSSEs) in supermolecular interaction energy computations of 10–20%.²⁶ When possible, we tried to avoid this by using a very large quadruple- ζ basis set in single-point calculations, which effectively eliminates the BSSE for common semi-local (hybrid) functionals. This is not the case for the double-hybrid B2PLYP,²⁷ which includes a fraction MP2 correlation and therefore converges more slowly toward the complete basis set (CBS) limit. In this case, we applied counterpoise corrections for BSSE.²⁸ All DFT calculations were carried out with the efficient def2-XVZP basis sets ($X = T$ or Q).²⁹

The D3-correction for long- and medium-range London dispersion effects is an atom pairwise method that takes into account the geometry of the molecule in the calculation of

the important C_6 dispersion coefficients.^{11,30} The correction can, for example, distinguish between aromatic and aliphatic carbon atoms, which is especially important here. Together with standard functionals, so-called DFT-D3 has been tested thoroughly for NCI and thermochemistry in many structurally very diverse systems.^{20,31,32} Compared with accurate WFT results, it provides a solid 5–10% accuracy for NCI energies. The same holds for recently tested (and readjusted) density-dependent nonlocal van der Waals functionals (termed DFT-NL). This method is based on developments of Langreth, Lundquist,¹⁵ and more recently Vydrov and Van Voorhis.³³ DFT-NL, which is based on this latter functional, has been tested thoroughly and yields excellent results.^{34,35} Similar to DFT-D3, the short-range behavior of the VV10 functional must be adopted to the “normal” semilocal functional to which it is added. We did so in ref 14 by readjusting the empirical parameter b in VV10 based on computations for the S22 benchmark set of non-covalent interaction energies. Whether the good performance of DFT-NL also holds for large aromatic systems will be investigated for the first time here.

The choice of the exchange–correlation functional in DFT is very important for normal thermochemical problems²⁰ but of less relevance for NCI when the functionals are properly dispersion-corrected. The TPSS³⁶ and revPBE³⁷ functionals are semilocal and therefore prone to so-called self-interaction error (SIE) and artificial charge transfer. In these cases, we performed calculations with the computationally more involved PW6B95³⁸ hybrid functional, in which 28% of semilocal exchange is replaced by nonlocal (SIE free) Fock exchange.

Estimated MP2/CBS values were obtained by extrapolation^{39,40} of correlation and SCF energies, employing huge aug-cc-pVTZ (aTZ) and aug-cc-pVQZ (aQZ) basis sets.^{41,42} The CCSD(T)/CBS results were estimated by employing a standard additivity scheme in which a correction from a small cc-pVDZ calculation is added to the MP2/CBS result.

$$E(\text{CCSD(T)/CBS}) \approx E(\text{MP2/CBS}) + [E(\text{CCSD(T)/DZ}) - E(\text{MP2/DZ})] \quad (1)$$

For a discussion of the accuracy of this approximation for small complexes, see ref 43. Based on this and previous works,⁴⁴ one can expect the accuracy of CCSD(T) energies obtained this way to be better than 5% for NCI. For small complexes, the error diminishes systematically when the size of the small basis in the above approach is increased

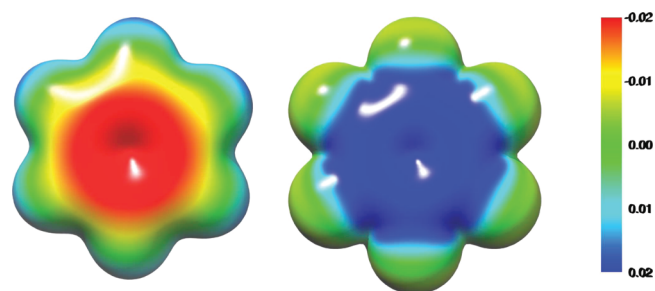


FIGURE 1. Electrostatic potential (the scale is in atomic hartree units = 627.5 kcal mol⁻¹) for benzene (left) and hexafluorobenzene (right) mapped on a 0.005 e⁻/bohr³ electron density surface based on TPSS/def2-TZVP calculations.

from DZ to, for example, TZ (leading to about 1–2% errors), but unfortunately, this is currently technically not possible for most systems studied herein.

In general, we will employ structures in subsequent single-point calculations that are fully optimized by DFT-D3 (typically using TPSS). These geometries are very close or even better than those computed by WFT like MP2, and we do not expect a significant impact of this choice on any of our conclusions.^{30,31}

3. Hexafluorobenzene Dimer and Hexafluorobenzene–Benzene Dimer

The stacked complex of hexafluorobenzene (HFB) and benzene is a prototype for the NCI of two electrostatically very different systems (i.e., oppositely signed quadrupole moments) and is therefore often used as a model in the literature.^{45,46} The difference is clearly visible in Figure 1, where maps of the ESP for the monomers are shown. From this simple, electrostatic picture, one could deduce that the perfectly stacked C_{6v} symmetric complex should be most favorable. In addition, the HFB dimer should show a parallel displaced geometry in order to avoid the Coulomb repulsion of two areas with similar ESP. However, this approach for understanding NCI is an oversimplification and does not lead to qualitatively correct results for the mixed dimer. Note further that combining the ESPs of two monomers to estimate their electrostatic interaction is physically wrong because the potential of one monomer interacts with the electronic and nuclear charges of the other (and not with the other ESP) and vice versa. Houk and Wheeler have also pointed out the pitfalls of using ESP plots for understanding stacking interactions.^{47,48}

In order to get insight into the interplay of electrostatics and dispersion in these two systems, we have investigated them further by employing energy decomposition analysis

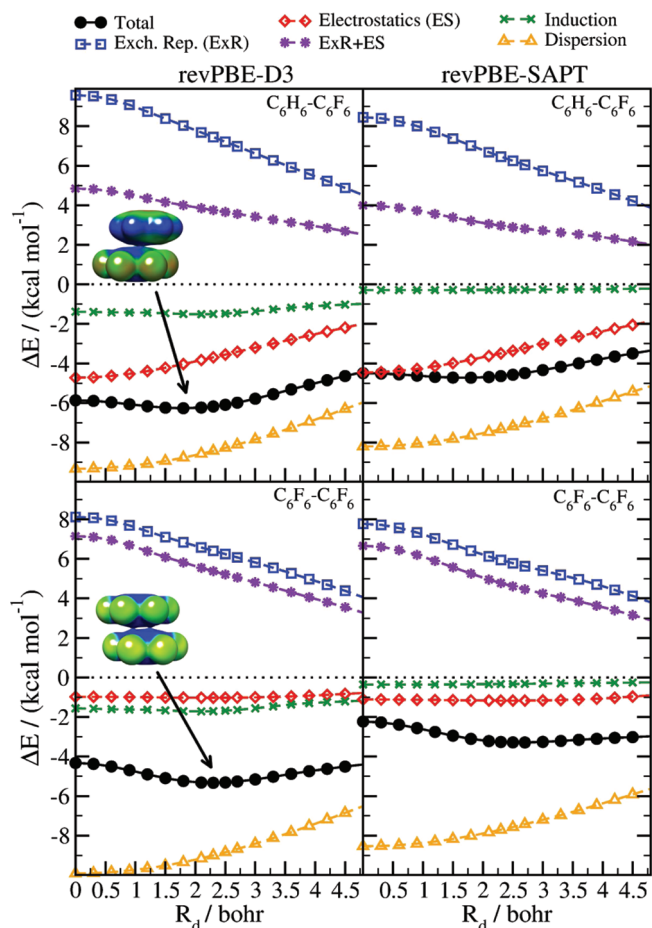


FIGURE 2. revPBE-D3 (left) and revPBE-SAPT (right) potential energy curves for the dimerization energy (ΔE) of the stacked hexafluorobenzene–benzene complex (top) and HFB dimer (bottom) for different parallel displacements (R_d) at a constant interplane distance of 6.5 bohr. The different contributions to the interaction energy are also shown. The colored ESP plots were done with the same parameters as in Figure 1.

(EDA⁴⁹) based on DFT-D3 as well as perturbative DFT-SAPT⁵⁰ calculations. We computed potential energy curves for the parallel displacement at a fixed interplanar distance. The DFT calculations were carried out on the revPBE-D3/def2-QZVP level, and the DFT-SAPT calculations were done employing the revPBE/aug-cc-pVDZ level of theory. The results are shown in Figure 2.

First of all, we note that quantitatively very similar results are obtained from the two very different (supermolecular vs fragment-based perturbation) methods, which can be regarded as a proof for the validity of our data. This is also notable because the SAPT calculations are computationally much more demanding than DFT-D3. The main differences are the reversed order of the electrostatics and induction curves for the HFB dimer and the slightly lower dispersion

contribution in the DFT-SAPT treatment. This “missing” dispersion and induction energy tentatively can be attributed to the small basis in the DFT-SAPT calculations. The features discussed in the following mostly apply to both methods.

The total interaction energy curves show that the minima for both dimers are parallel displaced. This is contrary to the predictions one would make from the plots in Figure 1. Furthermore, the minima are at very similar displacements (R_d), and the total interaction differs only by about 2 kcal mol⁻¹ (about 20–30%). One notable difference is the electrostatic interaction energy in the two cases. While it is mostly constant (but still attractive) in the HFB dimer, this is not the case for the mixed dimer. Here, the fully stacked conformation is electrostatically favored. However, this interaction is not able to completely overcome the contribution from exchange repulsion, which is also considerably larger in the mixed than in the HFB dimer. This leads to the parallel displaced minimum for the mixed dimer instead of the expected fully stacked geometry. Note, however, that the displacement potential is very flat (energy differences of about 1 kcal mol⁻¹, which is close to the thermal energy at room temperature).

In conclusion, this example shows that considering the electrostatic interaction alone can lead to qualitatively wrong predictions because the counteracting Pauli repulsion is not considered. Moreover, typical ESP plots show only part of the potential, which in total is represented by a much more complicated spatial integral. We recommend using ESP plots merely for a qualitative estimation of the polarity of the monomers and for giving first hints on their possible geometric arrangements. They should never be used for discussing relative energies on a few kcal mol⁻¹ scale.

4. Aromatic versus Aliphatic Interactions

Because van der Waals complexes are formed by almost all neutral, closed-shell molecules, one can wonder what should be so special about aromatic interactions compared with, for example, saturated (hydrogenated) rings of about the same size. This was investigated recently under the provocative title “Do special noncovalent π – π stacking interactions really exist?”.⁸ Later this topic was reinvestigated by Hohenstein and Sherrill employing SAPT.⁵¹

We consider this example here with a methodological focus. In the original work, it was already shown that the older DFT-D2 method shows systematic errors. The D2-dispersion correction⁵² makes use of fixed C_6 -dispersion

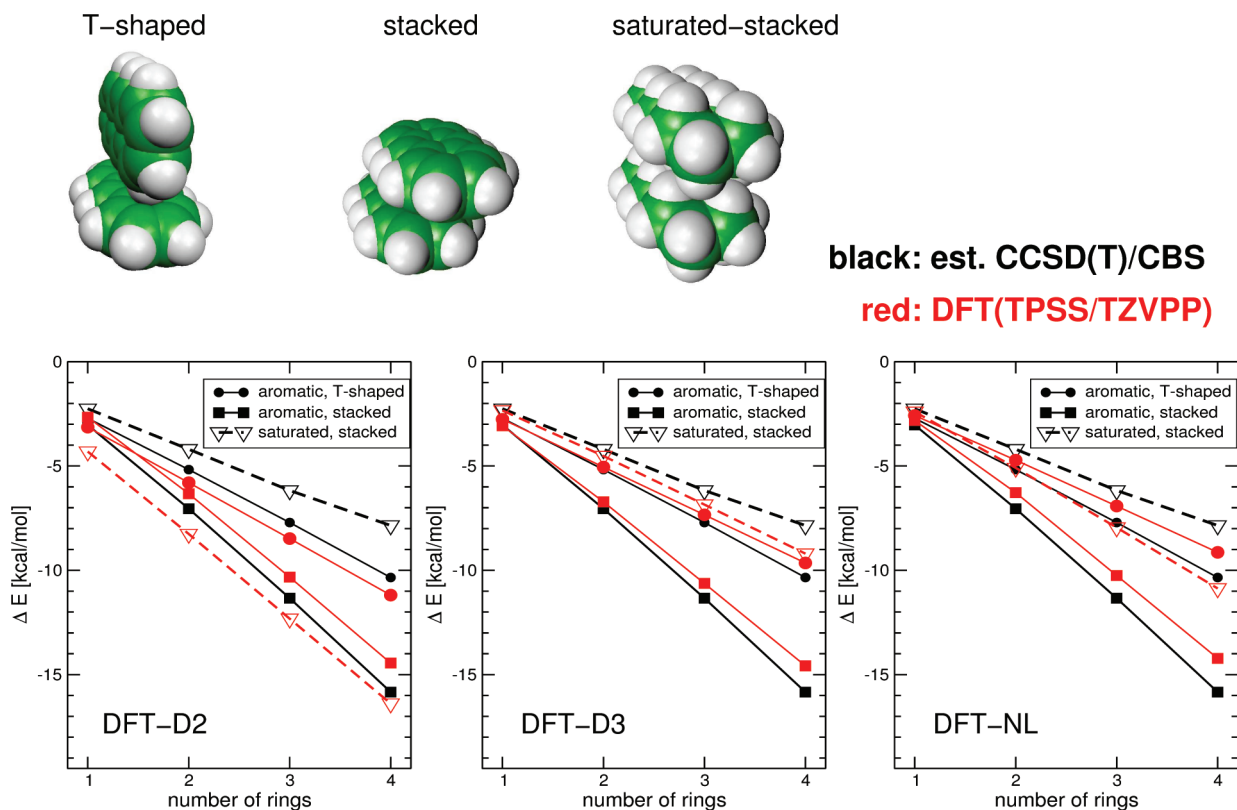


FIGURE 3. Dimerization energies of acenes and corresponding saturated rings for different molecule sizes. Black lines and symbols correspond to accurate reference values (est. CCSD(T)/CBS), while DFT/TPSS data are in red. The top of the figure shows the investigated structure motifs for three rings.

coefficients for all atoms of the same element so that changes of the hybridization state, for example, from sp^2 to sp^3 , are not accounted for. As will be shown below this effect is essential in order to distinguish aromatic from aliphatic interactions.

We take the linear condensed acenes from benzene ($n = 1$) to tetracene ($n = 4$) and the corresponding perhydrogenated rings as models. Homodimers of stacked aromatic and saturated as well as aromatic T-shaped orientation are investigated using the structures from ref 8 (see also Figure 3). According to the reference data in this figure, for one and two rings, there is little difference between the three binding motifs, i.e. stacked-aromatic and stacked-saturated. Interestingly, the T-shaped aromatic complexes always behave like the saturated ones, indicating that the close proximity in π -stacked arrangement is important.

For three and four rings, the interaction in the stacked aromatic case increases more strongly than for the other two binding modes, which show only a linear increase of interaction strength with a smaller slope. These features and in particular the strong preference for large aromatic molecules to stack is not described correctly by DFT-D2. This is more or

less independent of the density functional used (TPSS/def2-TZVPP data are shown). As can be seen in Figure 3, the theoretical description at this level is even qualitatively wrong because the stacked saturated complexes are most strongly bound.

This failure can be attributed to the same dispersion coefficients for sp^2 to sp^3 carbon atoms in the DFT-D2 method (30.4 au). In DFT-D3 and other modern dispersion corrections,^{12,13} these coefficients depend on the geometric or electronic environment of the atom in the molecule. In DFT-D3,¹¹ for example, the dispersion coefficients for sp^2 and sp^3 carbon atoms are about 25 and 18 au, respectively, corresponding to about 30% change due to hybridization. Interestingly, the DFT-NL method can also distinguish between the saturated and stacked aromatic systems, although we note a somewhat worse agreement with the reference regarding the relative stabilities of the T-shaped versus the saturated complexes.

Beside some effects of the different short-range treatment in D3 compared with DFT-D2, this is the main reason why DFT-D3 in Figure 3 shows the right qualitative picture and even a good quantitative agreement with the

TABLE 1. Dimerization Energies for the Porphyrin (D_{2h}) and Coronene Dimers^a

method	porphyrin dimer	coronene dimer
TPSS-D3 ^b	-11.0	-19.0
PW6B95-D3 ^b	-10.5	-20.5
B2PLYP-D3 ^b	-15.3	-22.7
TPSS-NL ^b	-13.1	-21.4
PW6B95-NL ^b	-10.9	-22.0
MP2/CBS ^c	-29.3	
SCS-MP2/CBS ^c	-19.9	
reference	-11.4 ^d	-20.0 ^e

^aB2PLYP values are counterpoise-corrected. All energies are in kcal mol⁻¹. ^bdef2-QZVP basis. ^cEstimated CBS(aTZ-aQZ), this work. ^dEstimated CCSD(T)/CBS, this work. ^eEstimated QCISD(T)/aTZ.⁵⁵

reference. Although not all the details in this system are described perfectly (the DFT-D3 aromatic curve is too linear and T-shaped and saturated complexes are slightly underbound), in conclusion, it is clear that dispersion corrections should be system-dependent in order to obtain accurate results for aromatic interactions in large systems.

5. Coronene and Porphyrin Dimers

The coronene and porphyrin dimers can be considered as intermediates on the way to more complex systems. While porphyrin is a good model for more extended stacking interactions in biological systems, coronene represents aromatic carbon materials like graphene sheets or carbon nanotubes.⁵³ While the dimers of these two compounds are already quite large, WFT-based results are still accessible in combination with extrapolation/additivity schemes. For porphyrin, we also had to make use of a highly symmetric conformer, because the reference CCSD(T) calculations would not have been feasible otherwise. Although this is certainly not the global minimum for the stacking (DFT-D2 computes a parallel displaced geometry⁵⁴), it is still bound and therefore an acceptable model to test methods, which, as usual, employ the same structures in the single-point computations.

For the coronene dimer, we used a parallel displaced (pd) conformation, which was found to be a minimum by Pulay and co-workers, who also published accurate QCISD(T) values for it.⁵⁵ We suggest the two dimers as models to evaluate the accuracy of DFT methods for larger, noncovalently bound systems. In order to do this, we carried out single-point calculations with different dispersion-corrected functionals: TPSS³⁶ (meta-GGA), the PW6B95³⁸ hybrid, and finally the double-hybrid B2PLYP.²⁷ The geometries were taken from refs 54 and 55, and the two schemes DFT-D3^{11,30} and DFT-NL¹⁴ are employed. In the case of DFT-D3, we also

applied an additional nonempirical three-body correction to the dispersion energy, because this contribution is non-negligible for larger systems.¹¹ The results and reference values are shown in Table 1. For comparison, we have also included MP2 and SCS-MP2⁵⁶ values for porphyrin as these methods are often employed in the literature for similar systems.

We first discuss the results for the porphyrin dimer. The most striking observation is the dramatic failure of MP2, which overestimates the binding energy by a factor of almost three. This is already known in the literature for smaller systems.^{7,8} SCS-MP2 improves the results to some degree. The error arises mainly from MP2 itself, because the results have been extrapolated to the CBS limit using two very large basis sets (the BSSE is expected to be smaller than 5%). The inherent error of MP2 for π -stacked systems is already evident from analysis of the benzene dimer and is attributed to the so-called uncoupled treatment of dispersion in MP2.⁵⁷

The DFT results are consistently much better than MP2 results and are close to the reference values. This is especially remarkable because two conceptually very different methods were applied to calculate the dispersion correction. The exception is B2PLYP-D3, which produces a slightly larger deviation. This is mainly a result of the inclusion of perturbative (MP2) correlation into the functional, because the large error from MP2 is to some degree inherited by B2PLYP-D3. However, the B2PLYP-D3 error is still one order of magnitude lower than the MP2 error. This additional virtual orbital dependent term is also the reason for the necessary counterpoise correction to the B2PLYP-D3 energies. While results from the other DFT functionals can be considered close to the CBS limit with the employed basis, the perturbative part in B2PLYP-D3 still suffers from some BSSE (the counterpoise corrections are 1.7 and 2.6 kcal mol⁻¹ for porphyrin and coronene, respectively).

The picture for the coronene dimer is similar, although B2PLYP-D3 is now more in line with the other functionals. One should also keep in mind that the error of the reference is estimated to be on the order of 5–10% of the binding energy, resulting from the limited basis used in the reference CCSD(T) calculations. We note further that three-body dispersion corrections are 1.9 and 2.9 kcal mol⁻¹ for the two complexes, which is clearly non-negligible if one aims at high accuracy.

In conclusion, this example shows that various standard functionals combined with two totally different types of dispersion corrections yield accurate interaction energies also for large stacked aromatic complexes. The typical

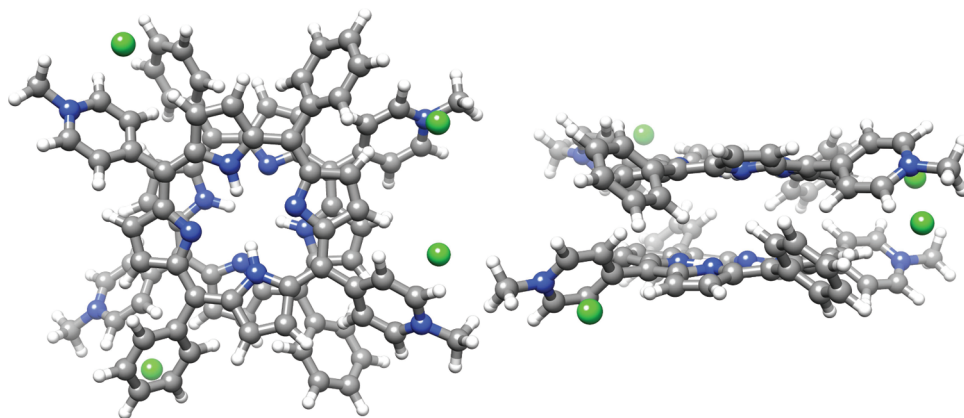


FIGURE 4. Top and side view of the 5,15-DiMPyP dimer including counterions.

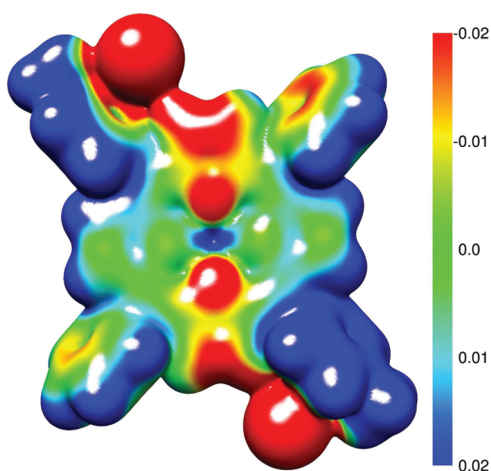


FIGURE 5. Electrostatic potential (the scale is in atomic hartree units) for the 5,15-DiMPyP monomer, including counterions, mapped to a $0.005 \text{ e}^-/\text{bohr}^3$ electron density surface. Density and ESP were calculated on the TPSS/def2-TZVP level of theory.

deviations compared with CCSD(T) results are 5–10% of the interaction energy, which is on the same scale as the remaining uncertainties in the reference treatments. MP2 should not be used for aromatic interactions.

6. Dimerization of a Charged Porphyrin in Water

There is solid experimental evidence that the 5,15-diphenyl-10,20-bis[4-(*N*-methyl)pyridinium]porphyrin dication (5,15-DiMPyP, Figure 4) forms dimers in water.⁵⁸ We have chosen this system to demonstrate the ability of modern quantum chemistry to accurately reproduce not only other theory (as in the benchmark above) but also experimental observables. This large system represents a further example where dispersion wins over repulsive Coulomb interactions as two dications form a stable quadruply charged complex in solution. In Figure 5, the ESP of the 5,15-DiMPyP monomer,

including chloride counterions, is shown. As noted above, we use it to get a feeling for the charge distribution. One clearly observes localized charges on the chlorides and slight delocalization from the formally charged parts into the porphyrin in agreement with chemical intuition. It should be mentioned that the potential in some regions is much higher than the plotting range (0.02 and $-0.02 E_h$, respectively). However, in order to get a reasonable description, we chose to keep the scale from Figure 1. This is a good example for the general problems with ESP plots that can easily be “tuned” in various directions by choosing the energy scale and the color coding. The NCI, and even electrostatic interactions, are too complex to be explained with the simple model of an ESP mapped onto an isosurface.

In order to correctly describe the complexation in solution, we have carried out several computations, following an *ab initio* scheme for obtaining free enthalpies of supramolecular complexes that we have recently developed.⁵⁹ Full geometry optimizations were carried out at the TPSS-D3/def2-TZVP level with the COSMO⁶⁰ continuum solvation model. For a realistic description one has to add counterions (chlorides) to the complexes, because the dimer is quadruply charged and otherwise would lead to unreasonable solvation (free) enthalpies. While optimizations of complexes with counterions are straightforward from the technical point of view, problems can arise in practice when their optimum positions (as defined by deep local maxima in the ESP) are not obvious from the electronic structure and many permutations must be tested. The resulting geometries were used to calculate the contribution of free energies of solvation to the complexation ($\Delta\delta G_{\text{solV}}$). This step employs the COSMO-RS solvation model.⁶¹ Gas-phase single-point complexation energies were obtained at the PW6B95-D3/def2-TZVP level (ΔE_{DFT} , $\Delta E_{\text{disp}}^{(2)}$). Again, three-body contributions ($\Delta E_{\text{disp}}^{(3)}$)

TABLE 2. Contributions to the Total Free Dimerization Enthalpy at 298.15 K^a

contribution	energy
ΔE_{DFT}	-18.5
$\Delta E_{\text{disp}}^{(2)}$	-34.6
$\Delta E_{\text{DFT-D3}}^{(2)}$	-53.1
$\Delta E_{\text{disp}}^{(3)}$	3.8
$\Delta E_{\text{DFT-D3, gas}}$	-49.3
$\Delta(E \rightarrow G)_{\text{RRHO}}$	24.6
ΔG_{gas}	-24.7
$\Delta(G_{\text{gas}} \rightarrow G_{\text{solv}})$	17.8
$\Sigma = \Delta G_{\text{calc}}$	-6.9
ΔG_{exptl}	-8.2

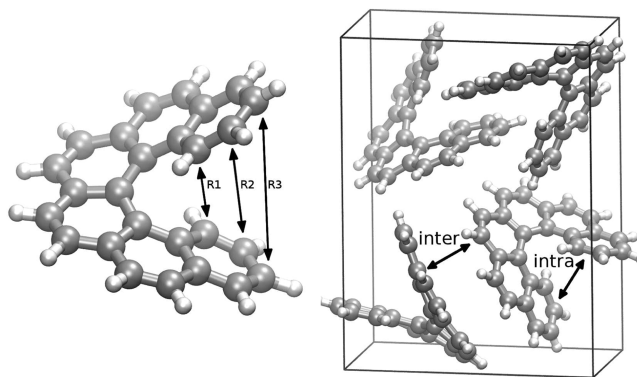
^aThe contributions (in kcal mol⁻¹) are added up from top to bottom.

were included in the calculation of the dispersion energy. Finally, we determined the sum of corrections from energy to free enthalpy in the rigid-rotor-harmonic-oscillator (RRHO) approximation (ΔG_{RRHO}) in the gas phase with the semiempirical PM6-D3H method^{59,62} (a detailed description of the whole scheme is given in ref 59). The results can be found in Table 2.

Interestingly, if one would equate gas-phase, dispersion-uncorrected DFT results (ΔE_{DFT}) with ΔG_{exptl} from solution (which is not uncommon in the literature), only the order of magnitude of the values is the same (-18.5 vs -8.2 kcal mol⁻¹). Quantitative agreement, however, cannot be obtained, and even the qualitative agreement is purely coincidental. As the data in Table 2 clearly show, there are canceling contributions of physically totally different origin involved. We propose to compute them individually as accurately as possible, and as can be seen, this eventually yields to an excellent agreement between ΔG_{calc} and ΔG_{exptl} (-6.9 vs -8.2 kcal mol⁻¹).

With added dispersion, the dimer becomes very strongly bound (-53.1 kcal mol⁻¹) in the gas phase, which is somewhat surprising when the large regions of positive ESP are considered. Clearly, dispersion wins over Coulomb repulsion here. However, the counterions are essential for a realistic simulation in solution as indicated by the huge repulsive interaction without them (gas phase value of 117.1 kcal mol⁻¹). Three-body dispersion is repulsive and contributes a significant correction of about 7%. After adding the rovibrational contributions to the free enthalpy, the dimer still remains strongly favored in the gas phase. This is partly quenched in water, but the computed free enthalpy of association remains negative. The computed and experimental values deviate by merely 1.3 kcal mol⁻¹.

Considering the complexity of the interactions in this example including aromatic stacking, screened but still

**FIGURE 6.** Intramolecular C-C distances as a measure for the twist and crystal packing of hexahelicene.**TABLE 3.** Intramolecular Structural Parameters of Hexahelicene^a

	R1	R2	R3
Isolated Molecule			
revPBE	3.28	4.60	5.65
revPBE-D3	3.17	4.43	5.46
Crystal			
revPBE	3.29	4.67	5.74
revPBE-D3	3.22	4.59	5.60
X-ray	3.22	4.58	5.63

^aAll values are given in Å.

strong Coulomb interactions, solvation and entropic terms, the quality of final result seems overwhelming. It strongly indicates that the right and most important physics of the process are modeled by the applied quantum chemistry.

7. Inter- and Intramolecular Aromatic Interactions in Hexahelicene

Helicenes are polycyclic aromatic hydrocarbons (PAHs) with a screw-shaped structure formed by ortho-annulated benzene rings.⁶³ Hexahelicene is used here as an example for PAHs, including intramolecular stacking. As in the previous case, we try to simulate the chemically relevant condensed phase, which is the solid in this case. In the molecular crystal of such a PAH inter- and intramolecular aromatic interactions (π - π as well as CH- π) are in subtle balance. In order to test dispersion-corrected DFT with nearly converged plane-wave basis sets and periodic boundary conditions for molecular crystals of aromatic compounds, we investigate how well three characteristic geometrical variables are reproduced. For recent studies of solids by DFT-D, see ref 64.

The pitch of the inner helix is measured by the distance of the two outermost atoms, defined as R1 in Figure 6.

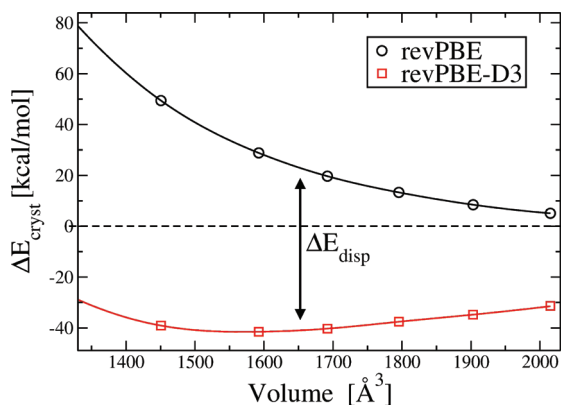


FIGURE 7. Potential energy curves of the crystallization energy of hexahelicene for different cell volumes.

This pitch is quite constant for most helicenes and is around 3.2 Å, while the outer pitch, defined by R3, varies depending on the size of the helicene⁶³ (5.63 Å for hexahelicene⁶⁵).

In Table 3, three carbon–carbon distances to describe the twist of the molecule (R1, R2, and R3, see Figure 6) are listed and compared with experimental values.

A dispersion-uncorrected gas-phase calculation with revPBE predicts a reasonable pitch of the molecule. The values are all close to the experimental ones, the largest deviation being 0.06 Å (see Table 3). However, this is not “the right answer for the right reason” because it is well-known (and clear from the previous examples) how important the inclusion of dispersion effects in DFT are for such PAHs. Again, compensation effects are at work that, however, can be clarified by realistic computations for the isolated molecule and the crystal. When intramolecular dispersion is “switched on”, the molecule contracts. The outer pitch (R3) decreases most, by 0.2 Å. Compared with the X-ray structure, these apparent deviations are considered as being very significant according to high *ab initio* standards.

However, it is clear that this is like comparing apples and oranges. When the PAH is surrounded by other molecules in the crystal, intermolecular interactions become almost as important as the intramolecular ones, which in turn influences the structure. In molecular crystals, these interactions are dominated by dispersion (and at short distances by Pauli-exchange repulsion), and flexible molecules can be “stretched” (see ref 66). In order to correctly describe these so-called packing effects, calculations have to be done for the solid. For hexahelicene, they are found to be only moderate. The molecule is slightly stretched by 0.16 and 0.14 Å for R2 and R3, respectively. Comparing the optimized and experimental crystal structures, we note a very good agreement as revPBE-D3

practically coincides with the X-ray data (largest deviation of 0.03 Å). In the dispersion-uncorrected revPBE solid-state calculation, all considered distances are significantly overestimated. In passing, we note that this is not a special property of the tested revPBE but common to many functionals.

Lattice parameters were also optimized. A fully relaxed potential curve for the crystallization energy (ΔE_{cryst}) with respect to the volume of the unit cell was calculated (see Figure 7). The crystallization energy is defined as

$$\Delta E_{\text{cryst}} = \frac{E_{\text{crystal}}^{\text{DFT(-D3)}}}{Z} - E_{\text{gas-phase}}^{\text{DFT(-D3)}} \quad (2)$$

where Z is the number of molecules per unit cell. For revPBE-D3, the minimum is found at about 1570 Å³, which is slightly smaller than the experimental volume of 1692 Å³. This structural overbinding can partly be explained by the neglected vibrational and thermal effects, which increase the volume. More important, however, is the potential for uncorrected revPBE, which is purely repulsive with no minimum for reasonable volumes. This and the positive ΔE_{cryst} value correspond to an unbound crystal state. On the contrary, the absolute of the revPBE-D3 result of $-38 \text{ kcal mol}^{-1}$ for the crystallization energy is very reasonable and in the ballpark of experimental sublimation enthalpies (ΔH_{sub}). Typical ΔH_{sub} values for PAH of this size are 30–40 kcal mol⁻¹.⁶⁷

In conclusion, this example shows that the asymptotically correct DFT-D3 method can also provide very good results for periodic systems in which the very long-range dispersion energy is more important than in molecules. With these tools, the solid state is accurately described and realistic comparisons between theory and experiment and investigations of crystal packing effects can be undertaken.

8. Conclusion

Dispersion-corrected DFT is able to correctly describe a wide variety of aromatic interactions, from model systems in the gas phase to free enthalpies in solution and the complex inter- and intramolecular interactions present in molecular crystals. DFT-D3 can offer, in combination with an energy decomposition analysis, detailed insights into the noncovalent interactions in aromatic systems. By comparison with SAPT calculations, it was shown that its energy components as computed with Morokuma-style energy decomposition analysis are physically sound. For systems of increasing size, DFT-D3 is still able to reproduce accurate WFT results within

an error of about 5–10%, which suggests it as an excellent candidate to investigate systems not accessible with standard WFT. This also applies to a certain extent to DFT-NL, but more research into this is essential for final conclusions. For larger, more dense systems, we conclude that three-body dispersion terms have to be taken into account for accurate results. In aromatic stacking interactions, and in particular if these are in competition or contact with saturated systems, it is crucial to employ methods that yield the correct C_6 dispersion coefficients for differently hybridized atoms. Finally, we shed some light on the interplay of dispersion and electrostatics. In an intriguing example, mainly the London dispersion interactions between two doubly charged porphyrin units can override strong Coulomb repulsion. While the plots of electrostatic potentials are valuable qualitative tools for understanding the charge distribution in fragments (as an alternative to population analysis), they should not be used to interpret the features of noncovalent interactions in detail. Although the theoretical description of aromatic interactions still contains challenging aspects (we mention here, for example, the not considered conformational/sampling problem in large structures), the future for accurate simulations in supramolecular or biological systems based on dispersion-corrected DFT seems bright.

9. Computational Details

The quantum chemical calculations were done with TURBO-MOLE (DFT-D3 and CCSD(T)/MP2),⁶⁸ Orca (DFT-NL),⁶⁹ MOL-PRO (SAPT),⁷⁰ MOPAC (PM6-D3H),⁷¹ and a modified version of VASP including DFT-D3 (periodic solid state calculations).^{72,73} For the DFT calculations carried out with ORCA and TURBOMOLE, we employed fine integration grids (m4/m5 in TURBOMOLE and grid5 in ORCA) and tight SCF convergence criteria. Where applicable, the resolution of the identity (RI) integral approximation^{74,75} was used. For carbon and hydrogen, the VASP standard PAW-potential was applied. An energy cutoff of 400 eV was taken. The Brillouin zone was sampled by a Γ -centered mesh of $(1 \times 1 \times 2)$ K-points. SCF and structure optimization convergence criteria of 10^{-6} eV and 10^{-2} eV/Å, respectively, were used.

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Stephan Ehrlich studied chemistry at the University of Münster. He received his diploma degree for his thesis about the development of benchmarking methods for DFT. Now he is continuing his

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FOOTNOTES

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