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A Benchmark Comparison of σ/σ and π/π Dispersion: the Dimers of Naphthalene and Decalin, and Coronene and Perhydrocoronene

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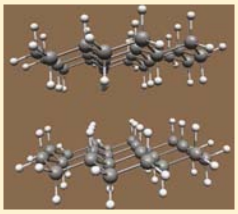
Supporting Information



ABSTRACT: The stacking interaction between π systems is a well-recognized structural motif, but stacking between σ systems was long considered of secondary importance. A recent paper points out that σ stacking can reach the energy of chemical bonds and concludes that "σ/σ and π/π interactions are equally important" (Fokin, A. F.; Gerbig, D.; Schreiner, P. R. *J. Am. Chem. Soc.* **2011**, *133*, 20036). Our analysis shows that strong dispersion interaction requires rigid subsystems and good fits of their repulsive potential walls, conditions which are satisfied for both graphenes and larger graphanes (perhydrographenes). Comparison of the dimerization energies of decalin and perhydrocoronene with those of the naphthalene and coronene dimers at the coupled cluster (CC) CCSD(T) level confirms the substantial σ-stacking energies in graphanes but shows lower binding energies than do the B97D calculations of Fokin et al. Graphane dimerization energies are substantially lower at the CC level than the corresponding π-stacking energies: the value for perhydrocoronene is only 67% of the value for coronene, and the difference increases with system size. Our best estimate for the dimerization energy of naphthalene is 6.1 kcal/mol. Spin-component scaled MP2 is unbalanced: it gives only 70% of the CCSD(T) binding energy in σ dimers. The B3LYP-D3 method compares very well with CC for both σ and π dimers at the van der Waals minimum but underestimates the binding at larger distances. We used the largest possible atomic basis for these systems with 64-bit arithmetic, half-augmented-pVDZ, and the results were corrected for basis set incompleteness at the MP2 level.

1. INTRODUCTION

Dispersion is a ubiquitous weak attractive force between molecules. It is always attractive, and thus it accumulates, and becomes one of the dominant forces for large molecules and supramolecular chemistry. Its calculation has received much attention lately because theory is finally able to deal with systems where dispersion is important. The classical Drude model accounts for dispersion qualitatively[1] but its quantum mechanical theory was developed only in 1930.[2] Hartree−Fock and local or semilocal density functional theories (DFT) are unable to account for genuine dispersion which does not require the overlap of the charge clouds of the interacting systems.[3] Heavily parametrized functionals[4] can reproduce the dispersive interaction near the van der Waals minimum well. However, they depend on the overlap of the densities which vanishes exponentially, and thus do not describe genuine dispersion which has an asymptotic R^{-6} distance dependence. The simplest theory that describes dispersion *for the right reason* is second-order Møller−Plesset perturbation theory (MP2). Unfortunately, MP2 significantly overestimates π/π-stacking energies.[5] Spin-component scaled MP2 (SCS-MP2)[6] gives excellent results for the benzene dimer[3,7] but overestimates π/π attraction for larger polycondensed aromatic hydrocarbons,[8,9] and, as we shall show, underestimates dispersion for σ systems. A simple way of introducing dispersion is to augment the energy by inverse power terms, multiplied by a damping factor at close interatomic distances to avoid divergence.[10] A number of dispersion-corrected DFT methods have been developed lately.[11a−i] The most widely used version is probably the DFT-D family of methods by Grimme,[11e,f,i] the latest version of which (DFT-D3)[11i] takes into account the hybridization state of the atoms involved.

The role of π stacking is well accepted in the literature. However, its analogue for saturated compounds, σ stacking, is relatively new, although it is well-known that all systems, σ or π, are subject to dispersion. Schreiner and co-workers have recently demonstrated experimentally and computationally that dispersion can be competitive with chemical bonding in stabilizing crowded σ-bonded systems.[12] Recently, the same group compared[13] association energies of perhydrographenes (graphanes) with the corresponding graphenes using dispersion-corrected DFT (mostly at the B97D level[11f]), and concluded that aliphatic−aliphatic and aromatic−aromatic dispersion interactions are essentially equal. This is surprising because simple models of dispersion[2] predict that the leading C_6 coefficient increases with the average localized orbital radius and decreases with the ionization potentials of the subsystems, both of which predict stronger attraction for π/π interactions at equal interatomic distances. DFT-D has an excellent cost−performance ratio but, as a semiempirical method, is not suitable for a benchmark. In this paper we discuss the qualitative features necessary for strong dispersion interaction and compare accurate calculated dispersion energies of two graphane dimers, the decalin (decahydronaphthalene, [10]-graphane) and perhydrocoronene ([24]graphane) dimers, with

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the corresponding naphthalene and coronene dimers.[8] Our results provide also an assessment of the performance of more affordable methods for dispersion: MP2, SCS-MP2,[6] and B3LYP-D3.[11i] Comparisons with long-range corrected DFT[14,15] will be published separately.

2. CALCULATION OF DIMERIZATION ENERGIES

Qualitative Considerations. The dispersion energy between small molecules is of the order of kT at room temperature, and thus thermal motion can disrupt the favorable attractive alignment in flexible molecules. Dispersion can compete with stronger forces only through cooperative action which requires that the monomers be rigid. To a large part, the prominence of π stacking is due not to inherently stronger dispersion but to the rigidity of π systems. Aliphatic molecules are generally flexible but larger graphanes, i.e., perhydrogenated graphenes, are quite rigid, and as demonstrated by Schreiner and co-workers,[12,13] they do not differ fundamentally from aromatic systems in dispersion strength. A second requirement for strong dispersive interaction is that the steep repulsive walls of the monomers should fit together well. The cause of the repulsion is Pauli exchange, and arises from the orthogonality requirement of overlapping orbitals. Its distance dependence is largely exponential. As the leading term of dispersion diminishes rapidly with the inverse sixth power of the intermolecular separation, significant dispersion requires close contact between the monomers. A simple model for the Pauli repulsion considers it proportional to the overlap of the monomer electron densities.[16,17] An even simpler model positions the repulsive wall at an isodensity surface, say with an electron density of ~0.01 e^-/a_0^3. If these walls fit together well, the two molecules can approach each other to the optimum distance, and the association energy will be high. Although it would appear that planar graphenes fit together perfectly, the electron density in aromatic molecules has maxima directly above the π atoms which destabilizes the sandwich structure and makes the graphite-like laterally displaced arrangement the most stable in larger graphenes. Note that arguments based on quadrupole−quadrupole interactions cannot account for the structure of larger graphenes or graphite. Graphanes also fit together quite well, with the axial hydrogens in one layer filling the cavity formed by three C−H bonds on the rear side of the axial hydrogen in the other layer. Mixed graphanes and graphenes fit together reasonably well, with the axial hydrogens of the graphane pointing approximately to the centers of the aromatic rings, in an arrangement similar to the methane−benzene van der Waals complex. The horizontal lattice constants of the two structures (~2.55 Å for graphanes, ~2.48 Å for graphenes) are close enough for a good fit in smaller, mixed complexes. For larger structures, however, the mismatch in the lattice constant prevents a good fit.

Computational Methods. We have determined the intermolecular association energies of the decalin and perhydrocoronene dimers and compared them to their respective aromatic analogues, the naphthalene and coronene dimers. The seven basic structures are shown in Figure 1. Our principal method is coupled cluster (CC), with single and double substitutions in the valence shell, and perturbative triples correction, using basis sets augmented with diffuse functions. This method, CCSD(T), is the most accurate routinely applicable level of electronic structure theory at present. For the coronene dimer we have used QCISD(T)[18] to maintain compatibility with our earlier results.[8] Our earlier calculations for benzene dimer[3] show that the difference between QCISD and CCSD is negligible (of the order of 0.01 kcal/mol). For most chemical applications QCISD and CCSD can be deemed equivalent. Our unpublished calculations show that even well-known examples of QCISD failures (see, e.g., ref 19) can be fixed if adequate basis sets are used. All calculations have been corrected for basis set superposition error (BSSE). Augmented atomic basis sets are necessary for calculating dispersion. However, when applied to larger systems, they become nearly linearly dependent, resulting in very large molecular orbital coefficients, predominantly in the virtual space. This leads to a severe loss of numerical accuracy, particularly for correlated calculations. The Hartree−Fock wave function, which uses only occupied orbitals, is usually stable; MP2, which uses integrals over two virtual orbitals, is worse, and coupled cluster and similar methods which use integrals over four virtual orbitals often become impossible using standard 64-bit arithmetic. Most programs (including PQS[20] which was used to carry out the calculations below) project out nearly redundant linear combinations from the basis set. However, this strategy fails for larger two- and three-dimensional (2- and 3-D) systems which have a dense manifold of nearly redundant functions. We had to use the *half-augmented* (ha-cc-pVDZ) basis set, as described previously for graphene dimers,[8,9] where augmentation functions are placed

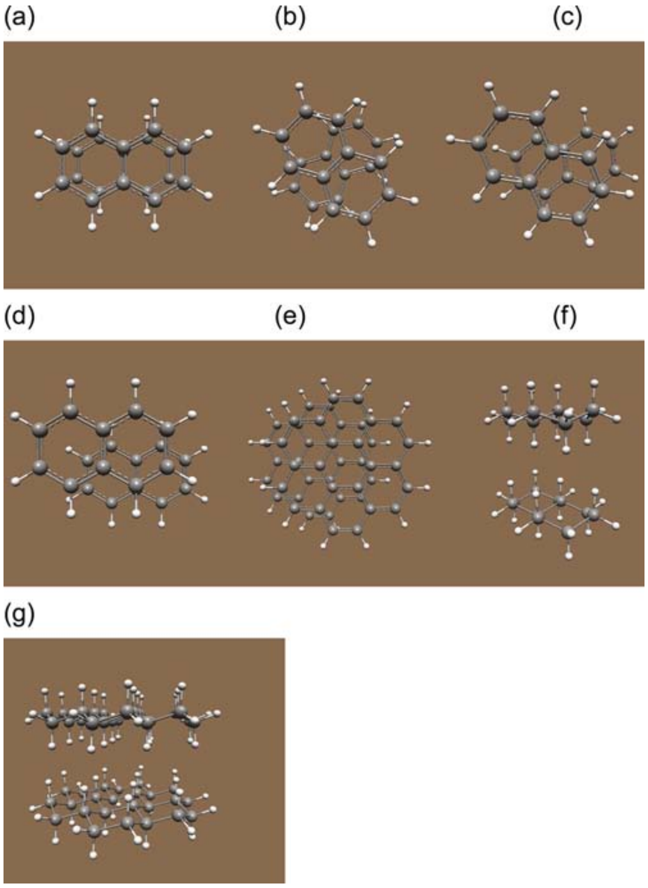

Figure 1. Geometries of seven basic systems under investigation: (a) sandwich naphthalene dimer, (b) crossed naphthalene dimer, (c) rotated−shifted naphthalene dimer, (d) graphite-like naphthalene, (e) coronene dimer, (f) vertically displaced decalin, and (g) perhydrocoronene dimer.

Table 1. CCSD(T) Geometries (in Å) and Binding Energies (kcal/mol) for π/π and σ/σ van der Waals Dimers[a]

dimer	x	y	z	MP2/ha-DZ (F12-MP2/aDZ)	SCS-MP2	SAPT (DFT)	CCSD(T)	ΔMP2 (DZ→TZ)	extrapolated CCSD(T)	B3LYP-D3
naphthalene sandwich D_{2h}	0.00	0.00	3.88	6.52 (6.95)	4.11		3.38	0.59	3.97	3.94
naphthalene cross D_{2d} (aTZ results)	0.00	0.00	3.63	8.70	5.615		4.76	0.72	5.48	5.69
naphthalene cross D_{2d} ref 32	0.00	0.00	3.60			5.51				
naphthalene PD (graphite) C_i	1.36	1.14	3.51	9.34 (10.13)	6.10		5.22	0.74	5.96	6.34
naphthalene C_i ref 32						5.62				
naphthalene rotated−shifted C_2	1.03[b]	−0.41[b]	3.53	9.81	6.33		5.31	0.81	6.12	6.50
decalin/aDZ C_{2h}	0.00	0.00	4.64	4.89	2.93		4.44	0.40	4.84	4.95
decalin/haDZ C_{2h}	0.00	0.00	4.67	4.68	2.83		4.24	0.51	4.75	4.94
perhydrocoronene D_{3d}	0.00	0.00	4.69	14.62	9.18		12.46	1.09	13.55	13.45
coronene C_{2h} ref 8	1.35	0.78	3.46	34.61	23.45		17.67	2.31	19.98	21.28
coronene C_{2h} ref 22	1.42	0.83	3.50			17.45				

[a] Using the ha-cc-pVDZ basis unless specified otherwise, after counterpoise correction, without zero-point energy. ΔMP2(D→T) is the energy difference between the MP2/ha-pVTZ and MP2/ha-pVDZ energies. The intermolecular geometries were optimized at the CCSD(T)/ha-cc-pVDZ level. The monomer geometries were kept fixed, see text. The x and y shifts are in the molecular plane, z is the monomer distance. [b] Values kept fixed from the SCS-MP2 optimized structure. The rotation angle of the two monomers is 45.5°.

only on every second carbon atom of an alternant hydrocarbon. No diffuse functions were placed on the axial hydrogens pointing outside in graphanes. This causes only negligible loss of binding energy. A correction for the residual basis set error was calculated as the difference between the MP2/ha-cc-pVTZ and MP2/ha-cc-pVDZ energies. This correction involves only high-lying, strongly oscillatory virtual orbitals and is only slightly affected by the shortcomings of MP2. We believe that the MP2-corrected CCSD(T) results are close to the basis set limit values. We have checked this by applying the same procedure to the benzene dimer, for which converged values are available.[3,7] The MP2-corrected CCSD(T)/ha-pVDZ dimerization energy of parallel displaced benzene differs from the large (aug-cc-pVQZ) coupled cluster result by less than 0.1 kcal/mol.

Calculations were carried out at monomer geometries optimized at the B3LYP/aug-cc-pVDZ level (aug-cc-pVTZ for naphthalene). The results are summarized in Table 1. The coupled cluster calculations in Table 1 are among the largest CCSD(T) calculations carried out to date. For instance, the perhydrocoronene dimer has 1440 basis functions and 264 correlated electrons. Besides the CCSD(T) calculations, MP2, SCS-MP2,[6] and B3LYP-D3[11i] calculations were also carried out with large basis sets. The performance of these methods will be compared in Results and Discussion.

To test the accuracy of the half-augmented basis, we have performed full CCSD(T)/aug-cc-pVDZ basis calculations for the decalin dimer which; unlike the naphthalene dimer, is still reasonably stable numerically. The results in Table 1 show that, after the MP2-level basis set correction, the ha-DZ and aug-DZ basis sets give virtually identical results. A test of the convergence of the MP2 correction was provided by MP2-F12 calculations for the naphthalene dimer. The F12 method uses interelectronic coordinates directly,[21] and is very efficient in approaching the basis set limit. These results (Table 1) show that our MP2 calculations are close to the basis set limit.

3. RESULTS AND DISCUSSION

Comparison of Graphanes and Graphenes. Our results give lower dimerization energies for graphanes than for the corresponding graphenes and thus do not support the conclusion of ref 13, on the basis of B97D calculations, that "σ/σ and π/π interactions are equally important". The binding energy of the decalin dimer is 78% of that of the naphthalene dimer, and the difference between aliphatic and aromatic systems increases with size. Our binding energy for of perhydrocoronene ([24]graphane) is less than 70% of the binding energy in the coronene dimer. We obtain virtually the same binding energy at the CCSD(T)/ha-pVDZ level as that of Podeszwa[22] using SAPT(DFT). Adding the MP2 correction increases our binding energy by 2.3 kcal/mol (13%). The simplest explanation of the discrepancy between refs 8 and 22 is that the nondiffuse bond functions used in the latter are not fully effective for dispersion. However, it is also possible that the perturbational components of our calculations, the (T) and MP2 corrections, slightly overestimate the correlation energy in low-bandgap systems such as coronene. Moreover, SAPT-(DFT) is also based on perturbation theory and is expected to be similarly affected. No such problem is expected for graphanes.

There is still some uncertainty about the correct value of graphene stacking energy. The only experimental value comes from the desorption energy of coronene from graphite.[23] Our calculations[9] gave an estimate of 32.1 kcal/mol (per C atom 1.34 kcal/mol or 58.1 meV) for the binding energy between coronene and circumcoronene, and 37.4 kcal/mol for the desorption energy which includes estimated contributions from the second and deeper layers of graphite. This supports the higher value given in ref 23, 1.5 ± 0.1 eV (34.6 ± 2 kcal/mol). Note that edge effects are still large for the coronene dimer which has a binding energy of only about 0.83 kcal/mol (36.1 meV) per C atom according to our calculations.[8] We have estimated the dimerization energy for large graphanes from B3LYP-D3 calculations on perhydrocoronene atop [54]-graphane ($C_{54}H_{72}$) and [96]graphane ($C_{96}H_{120}$), where edge effects are largely absent, to be 0.80 and 0.87 kcal/mol/C atom, respectively, i.e. only 65% of the aromatic value. Large graphanes are very well localized systems, and B3LYP-D3, which reproduces our CCSD(T) binding energies to 2% accuracy, should be adequate. The binding energy of 1.2 kcal/mol per C atom in ref 13 for an infinite graphane sheeet is too large in light of our results.

The Naphthalene Dimer. This system has been the subject of several earlier studies, but no CC calculations with augmented basis sets are available for the less symmetrical minima. The experimental binding energy of Gonzales and

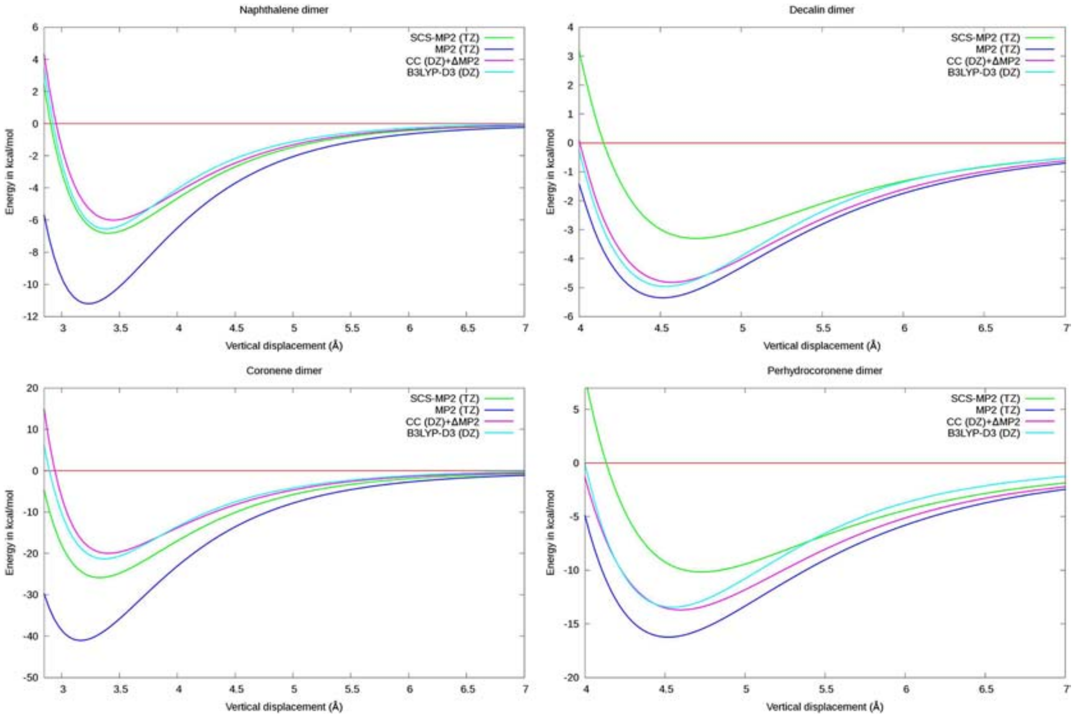

Figure 2. Potential energy surfaces as a function of interplanar distances (aromatic systems) or vertical shift (saturated systems) for two graphene-like systems (naphthalene and coronene) and two saturated graphane type systems (decalin and perhydrocoronene). All the results for MP2 and SCS_MP2 are calculated in half-augmented cc-pVTZ (haTZ) basis set, and the CCSD(T) values are given for extrapolated haTZ basis set (see text), while B3LYP-D3 plots are determined in aug-cc-pVDZ basis set. The vertical shift for the saturated systems is defined as a translation of one of the monomers in the direction of axial hydrogen atoms (a value of zero means that the monomers are exactly at the same position).

Lim,[24] 2.77 kcal/mol, is too low to correspond to a stacked dimer, even after zero-point correction. MP2, used in most early calculations[25a−d] overestimates the aromatic π−π-stacking energy[26] but the small basis sets used give a canceling error. The first CCSD(T) calculations, although with small basis sets, were performed by Tsuzuki et al.[27] Their final results were obtained from an elaborate correction scheme. The strongest binding, 5.73 kcal/mol was obtained for the graphite-like slipped parallel (C_i) form. This value agrees well with our direct determination in Table 1. Sato et al.[28] used a long-range corrected exchange-correlation potential in DFT, in conjunction with the Andersson−Langreth−Lunqvist (ALL) form of the dispersion interaction to determine the cardinal points on the benzene and naphthalene dimer potential surfaces. The ALL dimerization energies for stacked geometries are uniformly ~0.2 kcal/mol higher than ours. However, for larger graphenes, ALL appears to underestimate the dispersion energy.[9] Nachtigall and co-workers,[29] using a parametrized form of the CCSD(T)-DFT energy difference, obtained the strongest bonding, 6.23 kcal/mol for a slipped−rotated C_2 dimer; this value differs only by 0.1 kcal/mol from ours. Recent CCSD(T) calculations with augmented basis sets are restricted to high-symmetry geometries.[30]

We have determined the minima on the naphthalene dimer potential surface at the CCSD(T)/ha-cc-pVDZ level. The results are shown in Tables 1 and S1 in the Supporting Information. Our binding energies for the sandwich (D_{2h}) and crossed (D_{2d}) forms are smaller than those of Mackie and DiLabio[30] because we use the full counterpoise correction while ref 30 uses only half of it. We have found that the infinite basis limit is best approximated by taking about 85% of the BSSE. The large-basis SAPT-DFT[31] results of Podeszwa and Szalewicz[32] for the crossed and graphite-type dimers, 5.51 and 5.62 kcal/mol, compare well with our values. The unrestricted minimum of the stacked naphthalene dimer at the SCS-MP2 level is a shifted−rotated structure with C_2 symmetry, similar to the PD-1 structure of ref 29. We have reoptimized the separation of the ring planes (z) and the rotation angle between the planar monomers at the BSSE-corrected CCSD(T)/ha-cc-pVDZ level (Figure S1). This structure is marginally (by 0.16 kcal/mol) more stable than the lowest graphite-like structure.

Comparison of Methods. CCSD(T) scales steeply with the seventh power of molecular size, and it is thus limited to benchmarking other, less expensive techniques. Local versions of CCSD(T) can reduce this steep scaling but they are not appropriate for comparing the very well localized graphanes with graphenes which have delocalized π orbitals. MP2 and SCS-MP2[6] scale with system size as $O(N^5)$. Symmetry-adapted perturbation theory SAPT, scales as $O(N^6)$. However, its DFT-based version, SAPT(DFT),[32] can use density fitting efficiently, diminishing its scaling to $O(N^5)$.

MP2 overestimates the stacking energy of the naphthalene dimer by almost a factor of 2 but it is close to the CCSD(T) values for the saturated compounds. SCS-MP2 is quite successful for the aromatic compounds but gives only about 60% of the binding energy for the decalin dimer, and is thus cannot be considered as an inexpensive alternative to CCSD(T).

Transferability-based semiempirical methods like B97D and B3LYP-D3 are fundamentally unable to describe nonlocal effects, such as the diminishing bandgap which is particularly critical in graphenes because they become a semi-metal in the infinite limit. This should lead to an increase in the dimerization energy not just in absolute value but also *per C atom*. In spite of this, B3LYP-D3 reproduces the CC calculations well for our test systems, including the coronene dimer. The DFT-CCSD(T) method also performs very well for π stacking, but it has not yet been developed for σ systems. B97D overestimates both π-stacking and σ-stacking energies, particularly the latter, as it does not distinguish between σ and π atoms. The B97D dimerization energy of perhydrocoronene is 26 kcal/mol,[13] almost double our extrapolated CCSD(T) value, 13.5 kcal/mol. Our results show that the B3LYP-D3 method[11i] offers uniform performance for both graphanes and graphenes near the van der Waals minimum. However, B3LYP-D3 underestimates the binding energy at larger (∼1.5 Re) distances (see the next paragraph). The energies in Table 1 were obtained at the CCSD(T) intermolecular geometries. B3LYP-D3/ha-cc-pVDZ optimized energies are given in Table S3 of the Supporting Information. Vazquez-Mayagoitia et al.[33] have tested the B97D method for small nonbonded systems[11f] and found good agreement with accurate calculations. However, as our comparison with ref 13 shows, B97D strongly overestimates σ interactions in larger systems.

As a final test of the performance of various methods, comparison was made of potential energy surfaces at B3LYP-D3, SCS-MP2, and MP2 level of theory with CCSD(T) benchmark data (Figure 2). Both SCS-MP2 and MP2 methods provide a uniform description of the interaction energy compared to CC values; i.e. the magnitude of the underestimation or overestimation of the interaction is roughly the same for all the distances. It means that both MP2 and SCS-MP2 curves are similar to that of CCSD(T), being only scaled or shifted, depending on the system in question. This is not the case with B3LYP-D3. It performs very well for equilibrium geometries, predicting both the distances and binding energies correctly, but it underestimates the binding at larger distances for all the investigated systems. Note that in all the plots presented in Figure 2, at some distance the B3LYP-D3 curve intersects the CCSD(T) curve. The binding energies predicted near the equilibrium distances are usually slightly below the CCSD(T) values, while they are above CCSD(T) for larger distances. This may be caused by slightly unbalanced descriptions originating from terms proportional to R^{-6} and R^{-8}, with the contribution of the R^{-6} terms slightly underestimated (and the R^{-8} term overestimated). This is an important observation as the D3 approach, in order to be applicable to arbitrary molecular systems, must properly describe the interactions for all distances. Although the attractive energy diminishes steeply with increasing distance, the number of contributions from distant interatomic pairs increases. A slight underestimation of long-range interactions leads to an underestimation of the binding energies for large van der Waals complexes. Indeed, it appears that this is already the case in perhydrocoronene dimer, where, in contrast to decalin, the B3LYP-D3 minimum energy is slightly above the CCSD(T) value. B3LYP-D3 underestimates the binding energy of the perhydrocoronene dimer at larger distances quite strongly, more than for decalin. The coronene dimer does not suffer from this kind of problem yet. The reason is probably that the binding in the perhydrocoronene dimer contains more contributions from distant atom pairs.

A single plot containing benchmark potential energy surfaces for all the systems under investigation is shown in Figure 3. Note that, although the definition of a vertical displacement for saturated and aromatic systems is essentially identical (see Figure 2), the same vertical shift does not result in equivalent interatomic distances. The vertical displacement in the case of an aromatic system defines the closest distance between any pair of atoms belonging to both monomers, while the same vertical displacement for a saturated system results in many close-lying hydrogen−hydrogen and hydrogen−carbon pairs.

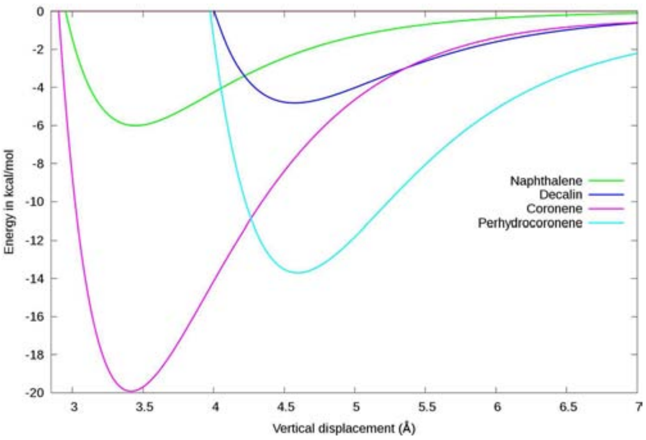

Figure 3. Extrapolated CCSD(T)/ha-pvDZ+ΔMP2(DZ→TZ) potential energy surfaces for all the systems presented on Figure 2. The result for coronene dimer is calculated at the QCISD(T) level of theory. For a definition of vertical shift (displacement) in saturated systems see Figure 2.

4. CONCLUSIONS

Coupled cluster calculations confirm the substantial dispersion interaction between larger (and therefore more rigid) graphanes, but this is still substantially lower than analogous π-stacking energies. Our best estimate for the π-stacking energy of large graphenes is 1.34 kcal/mol (58.1 meV) per carbon atom. The corresponding σ-stacking energy in large graphanes is estimated to be 0.87 kcal/mol (37.7 meV). MP2 significantly overestimates π-stacking energies. SCS-MP2[6] is quite accurate for smaller graphenes but underestimates σ-stacking energies and overestimates dimerization energies for larger polycondensed aromatic hydrocarbons. SAPT(DFT) agrees generally very well with CCSD(T) but gives a somewhat lower dimerization energy for coronene. B3LYP-D3[11i] is a low-cost method that reproduces our CCSD(T) results very well, especially near equilibrium distances. Dispersion can be competitive with stronger forces if the monomers are rigid and their respective Pauli repulsion surfaces fit together well. Although the interaction between saturated analogues of aromatic hydrocarbons is surprisingly strong, it might be attributed to the proximity of axial hydrogen atoms. The predicted equilibrium distance between the average planes in perhydrocoronene and decalin is about 4.7 Å. This is much longer than in the coronene dimer, but individual separation between the closest hydrogen atoms is only about 2.5 Å, and the closest carbon atoms are separated by about 4.5 Å. This makes it difficult to directly compare the relative strength of the dispersion energies between graphanes and graphenes, even at larger distances, as the differences result from both different molecular electronic structure and different molecular geometry.

■ ASSOCIATED CONTENT

Supporting Information

Additional tables with Hartree−Fock energies, triples contributions, optimized B3LYP-D3 geometries and energies, Cartesian coordinates and CCSD(T) total energies, a figure with the global minimum structure of the naphthalene dimer, and a table with polarizabilities for naphthalene and decalin. 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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