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Performance of the Empirical Dispersion Corrections to Density Functional Theory: Thermodynamics of Hydrocarbon Isomerizations and Olefin Monomer Insertion Reactions

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Abstract: Most of the commonly used approximate density functionals have systematic errors in the description of the stability of hydrocarbons. This poses a challenge for the realistic modeling of reactions involving hydrocarbons, such as olefin polymerization. Practical remedies have been proposed, including the application to usual black-box DFT of additional empirical correction CR^{-6} terms for the van der Waals interaction (termed DFT-D), or introducing additional pseudopotentials that introduce some medium-to-long-range attraction (C-Pot). In this Article, we use the DFT-D scheme as realized in our BOptimize package to evaluate the performance of a range of commonly used DFT functionals (combinations of xPBE, B88, OPTX with LYP and cPBE GGAs and hybrids) for the modeling of the thermodynamics of reactions of the growth of common polyolefins. We also review and reproduce some of the previously done benchmarks in the area: alkane branching and relative stability of $C_{12}H_{12}$ and $C_{10}H_{16}$ isomers. In addition to the common DFT methods, computations with correlated wave function methods (MP2) and the new functionals B97-D and M06-L were performed. The performance of the special density functionals B97-D and M06-L is, in general, similar to the best DFT-D corrected regular functionals (BPBE-D and PBE-D). The results show that (1) the DFT-D correction is sufficient to describe alkane branching, but its performance depends on the parametrization; (2) inclusion of the correction is essential for a proper description of the thermodynamics of reactions of polymer growth; and (3) not all approximate density functionals perform effectively for the description of hydrocarbons even with the correction. The C-Pot method for the B3LYP functional shows quantitatively correct results for our test cases. The enthalpies of hydrocarbon reactions were analyzed in terms of the repulsion characteristics of a given DFT method. PBE is the least repulsive, while OLYP is the most. However, there are cases where the failure of a DFT method cannot be correlated with its repulsive character. A striking example is the performance of B3LYP and BLYP for caged molecules with small carbocycles, such as the $[D_{3d}]$-octahedrane. The stability of $[D_{3d}]$-octahedrane is underestimated by the B3LYP, BLYP, and B97-D functionals, but not by DFT methods that contain either B88 exchange or LYP correlation functionals separately. While DFT-D cannot amend the performance of the former functionals for the octahedrane, C-Pot for B3LYP does.

Introduction

Density functional theory (DFT) methods are the most frequently used tools in today's theoretical chemists' inven-

tory. After the introduction of the generalized gradient approximation (GGA),[1,2] and, later, the advent of hybrid density functionals,[3] it became a black-box computational method for the majority of chemists.

However, recently some flaws in the commonly used black-box density functional methods were exposed. These failures came as a surprise in part because the methods have

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been thoroughly tested on sets of small molecules like those included in the G1, G2[4,5] benchmark sets. In recent years, progress of both computer hardware and DFT software (such as resolution of identity fitting techniques[6−8]) allowed for the routine treatment of systems containing up to a few hundred atoms. It turned out that density functionals (DFs) that did well for the G1 set, most notably B3LYP, can systematically fail to describe larger systems. By now, extensive literature exists on benchmarking of the performance of different DFs for a range of problems.[9−23]

One of the problematic areas for DFT is the description of the stability of hydrocarbons.[24] Schleyer and co-workers did several tests comparing isomeric polycyclic hydrocarbons.[14] Schreiner ascribed errors in calculations of isodesmic reactions to the failure of DFT to describe "protobranching" (1,3 attractive interactions) for linear hydrocarbons.[16,17] Grimme studied alkane branching as a testing ground for his methods.[12,25] These studies show that the majority of modern DFs has problems with the description of both intermolecular and intramolecular interactions in hydrocarbons. An example of the former problem is the failure of most GGA and hybrid functionals to predict the structure of the benzene shifted stacking dimer. Intramolecular issues appear when comparing branched and linear alkanes (*n*-octane vs 2,2,3,3-tetramethyl-butane). Often the simple local density approximation functional performs better than either GGAs or hybrids, giving, unlike the latter, qualitatively correct results.[10] The variability in the performance of different DF methods even led to the proposal of multilayer QM/QM computations employing several different DFs for different parts of the model system,[26] picking a functional that performs best for each particular type of interaction within the system.

A few explanations of these deficiencies and remedies for them have been proposed. On the basis of the analysis of MP2 pair correlation energy in branched hydrocarbons, Grimme coined the term "medium-range correlation energy" for the interaction energy that is not described well with GGA.[12] Yang et al.[27] traced problems of common DFs to the delocalization errors. They also noted, comparing potential energy curves of interaction between two methane molecules, that most GGAs (especially with the Becke88[1] exchange) are too repulsive as compared to CCSD(T) at shorter intermolecular distances. They suggested that for modeling of the formation of highly branched or polycyclic molecules, functionals with minimal delocalization errors such as PBE1 should be chosen.

Grimme, in his 2004 work,[28] proposed a simple empirical CR^{-6} correction term (with coefficients obtained from ab initio calculations) for the long-range van der Waals (vdW) interactions, together with a damping function that turns it off at shorter distances. He applied this correction to several hydrocarbon test cases and stated that the correction alone is not enough to describe energy differences for the *n*-octane branching for GGA functionals such as PBE and BLYP. One of Grimme's proposals was to use his double-hybrid functionals containing some MP2 corrections (see ref 13 for leading references); together with the dispersion corrections (but not without them) they describe alkane branching very
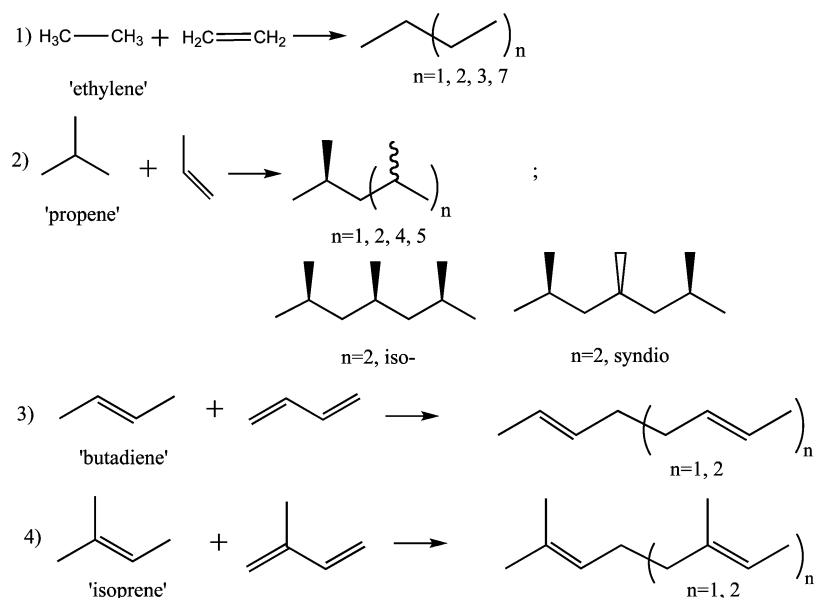
successfully. Later, however, he revised his dispersion correction approach.[29] Following him, we call this revised approach DFT-D hereafter. In the 2006 paper, Grimme also introduced a new parametrization of the power-series B97-type[30] density functional,[29] B97-D that, together with the dispersion correction, gave the correct sign for the alkane branching. However, simple DFs were not thoroughly tested at that time with the new DFT-D parametrization (or at least this was not reported in the paper). The widely cited (for example, see refs 16 and 31) result, based on the old DFT-D parametrization, that BLYP-D and PBE-D are insufficient for the description of nonbonded interactions in alkanes, does not necessarily hold with the new DFT-D parameter set.

It soon became obvious that the character of the damping function is at least as important as the choice of the dispersion coefficients, for it acts in the crucial medium-range region. Head-Gordon proposed to use a power-twelve term instead of an exponential in the denominator of the damping function, otherwise following Grimme's approach.[29] Ducere and Cavallo introduced a parametrization of the damping function for intermolecular interactions of DNA base pairs.[32] Recently, Cornimonbeauf and co-workers reparametrized the DFT-D damping function of the latter work to accurately describe both intra- and intermolecular molecular interactions in alkanes.[33]

An alternative to the addition of an empirical correction is modification of core−core interactions within the DFT method itself. One of the computationally cheapest and most readily available methods for it is to modify (or add) a pseudopotential that would introduce some medium and long-distance attractive interactions to the energy, thus emulating the dispersion. The pseudopotential is usually parametrized to reproduce structures of a training set of intermolecular complexes. First introduced for the solid state computational chemistry for plane-wave computations by Röthlisberger et al.,[34,35] it was extended by DiLabio to molecular Gaussian basis set computations, and named the C-Pot method (because they only used a pseudopotential on carbon).[36] The C-Pot method was shown to help to describe intermolecular interactions of some condensed aromatics dimers such as coronene and graphene sheets. We note that the pseudopotentials are both basis set and density-functional dependent and have to be parametrized by molecular calculations. Thus, they are "less ab initio" than Grimme's DFT-D method that is based on atomic parameters and has only the global scaling factor for each density functional to be fitted.

While the ad-hoc CR^{-6} dispersion correction of DFT-D can (as we will show later) indeed be very beneficial for energies of hydrocarbons, it can be problematic in cases where there can be strong changes in atomic oxidation states and hybridization. A more sophisticated method for the representation of the dispersion corrections to DFT (see refs 21, 37 for examples and leading references) might be free from these shortcomings. However, at present such methods are not widely available; also usually they rely on fitting to molecular data, which are not always available.
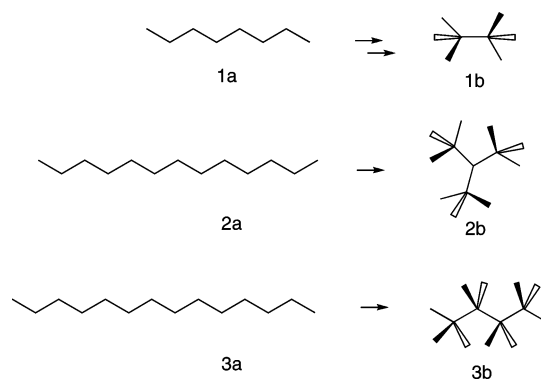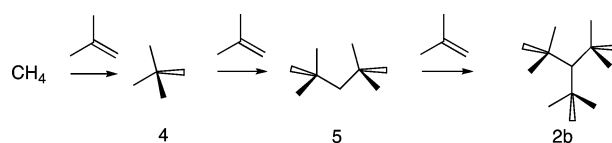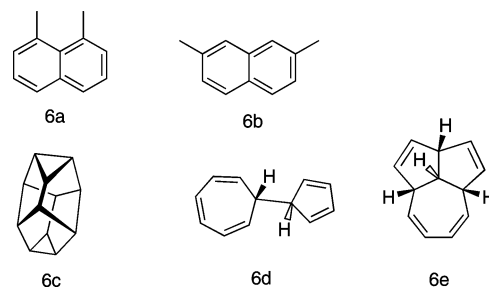
Modeling of organometallic catalysis (which was one of the first and the most remarkable successes of DFT) with a realistic model system should include adequate representation

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Scheme 1. Polymer Growth (Monomer Insertion) Reactions

Scheme 2. Alkane Branching Reactions

Scheme 3. Addition of *t*-Bu Groups to Methane

**Scheme 4.** Isomers of $C_{12}H_{12}$ Hydrocarbons

of the catalysts' ligands, weak complexes of reactants with the catalyst, and, for the case of polymerizations, accurate modeling of the growing chain. For example, we have shown in the case of an expanded porphyrin complex[38] that the inclusion of peripheral alkyl substituents in the model complex is important for the description of the complex's electronic and geometric structures. Many of the popular organometallic ligands (a good example is penta-methyl-cyclopentadienyl) are hydrocarbons themselves and/or have multiple hydrocarbon peripheral substituents that might interact with each other, with other ligands, as well as with reactants during the course of reactions. Thus, if we want to treat realistic model systems with DFT (which is usually the only affordable choice), we need to assess the accuracy of the method.

In the present study, we apply Grimme's dispersion correction together with selected commonly used density functionals to larger hydrocarbon systems, considering the accuracy of predictions of the thermodynamics of the olefin polymerization. In addition, within the same approach, we study other model systems from the literature, such as alkane branching and polycyclic hydrocarbon isomerizations. We compare our results to computational data from the literature, by reproducing selected cases from refs 12, 14, 17, 28, 29, and to experimental results. Where the latter are unavailable, we will use ab initio correlated methods (MP2). The systems under study are shown in Schemes 1−5. Unlike several previous studies dedicated to DFT performance, we aim to model not just isodesmic or homodesmotic reactions (which can indeed be used for obtaining valuable thermodynamical information as well as insights into method performance; see, for example, the recent work of ref 39), but systems of more practical, chemical relevance.

Our primary aim is to assess whether a black-box density functional method using a common, readily available density functional together with the simple DFT-D dispersion corrections is reliable for the description of larger hydrocarbon systems including systems with different degrees of sterical strain. Other options, besides black-box DFs and Grimme's DFT-D, were used for comparison. Specifically, we have tried the newly developed "dispersion-aware" density functionals B97-D and M06-L. The C-Pot method by DiLabio was also investigated. Others have already studied some of the test systems we use

Scheme 5. Isomers of $C_{10}H_{16}$ Hydrocarbons
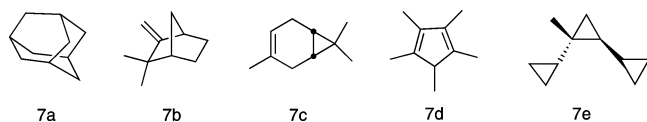
individually, but as far as we know they have not been systematically considered together.

In general, our results show that common GGA and hybrid density functionals yield rather poor results for olefin polymerization energies. Properties like the energies of alkane branching are similarly predicted incorrectly. The performance of a particular DF for olefin polymerization or alkane branching can be traced to its repulsive character; the "harder" the functional is, the larger is the error. In these cases, the functionals can be improved by applying the DFT-D correction that fixes over-repulsiveness or under-attractiveness. Generally, the DFT-D correction is also beneficial for the description of other hydrocarbon isomerizations. The alternative pseudopotential modification method C-Pot is shown to yield improved results for B3LYP.

Computational Methods

In the DFT-D approach, the attractive C_nR^{-n} correction terms for the "dispersion interaction" are simply added to the total DFT energy. To avoid undesirable interference of the correction terms with the DFT energy at short distances, a damping function is used. The correction by Grimme[29] we use in the present work uses only C_6R^{-6} terms and has the form of eqs 1 and 2:

$$E_{\text{total}} = E_{\text{DFT}} + E_{\text{disp}} \tag{1}$$

$$E_{\text{disp}} = -s \sum_{i=1,N}^{N} \sum_{j=1,i-1}^{N} F_{\text{damp}}(R_{ij}) C_6^{ij} R_{ij}^{-6} \tag{2}$$

The global scaling factor s is optimized for each functional. In Grimme's 2006 method,[29] the atomic van der Waals coefficients C_6^i are obtained from atomic properties as $C_6^i = 0.05NI\alpha$. Here, I is the ionization potential, α is the static polarizability of the atom, and N is the number of electrons in the next noble gas in the elements' period. Coefficients C_6^{ij} were then set to the geometric mean of C_6^i and C_6^j. The damping function used is

$$F_{\text{damp}}(R_{ij}) = \frac{1}{1 + e^{-a(R_{ij}/R_0^{ij}-1)}} \tag{3}$$

with $a = 20$; atomic radii R_0^{ij} are based on DFT computations for elements up to Xe with a scaling factor of 1.1 applied. Thanks to the universality and ease of use of this approach, the DFT-D correction in its Grimme-2006 form has been implemented in recent releases of many popular quantum-chemistry codes, such as, to name a few, ADF, GAMESS-US, and Gaussian 09.

Some exchange functionals are known to be less repulsive than others, and thus the DFT-D correction might overcompensate for the dispersion if used together with "too attractive" functionals. Grimme in 2006[29] and Head-Gordon

in 2008[40] developed their parametrizations of the Becke-1997[30] power-series GGA specifically parametrized including DFT-D corrections, thus avoiding the dispersion double-counting that is otherwise handled by the scaling factor s only. Head-Gordon also used an inverse power-twelve damping function instead of Grimme's exponential one (see the Supporting Information). The choices of parametrization of the global scaling coefficient s versus scaling of the R_0 atomic parameters within the Grimme-2006 scheme were systematically explored in the recent work of Baldridge.[41]

Because the form of the correction does not depend on the underlying quantum-chemical method, it is straightforward to code it as an external routine, thus avoiding possible limitations of any given QM program package. We have implemented the DFT-D corrections for energies, gradients, and second derivatives of the energy in the stand-alone optimizer code BOptimize.[42] The code is now interfaced to many DFT and ab initio packages. Most of the results presented here were obtained with it.

While there are many approximate density functionals, the emphasis of this work is on practically available and computationally efficient solutions that are or have the potential to be widely used. For that reason, we chose to test the local functional VWN5[43] (with Slater exchange), and the GGA functionals BLYP,[1,2] PBE,[44] and its modifications by Adamo and Barone MPBE,[45] BPBE,[1,44] and OLYP.[2,46] All of these are local GGA functionals, and as such allow for the most efficient use of Coulomb and exchange fitting techniques. For comparison, the two popular hybrid functionals B3LYP[3] and PBE1[47] were also included; to specifically test the effect of increasing the amount of exact exchange in the latter, the HFPBE combination with PBE correlation and 100% exact exchange was also tried in selected cases. Calculations using the functionals listed above were performed with the Priroda code version 6 with nonrelativistic all-electron general-contracted Gaussian basis sets.[8,48,49] For DFT calculations with Priroda, the L11 basis set ((6s,2p)/[2s,1p] for H, (10s7p3d)/[4s3p1d] for C, roughly corresponds to the popular cc-CVDZ basis) was used along with the corresponding auxiliary fitting set. RI-MP2 calculations were performed in the larger L2 set ((8s4p2d)/[3s2p1d] for H, (12s8p4d2f)/[4s3p2d1f] for C, roughly corresponds to the popular cc-pVTZ basis).

Geometries were fully optimized at the DFT or MP2 levels of theory. For GGA DFTs, analytical second derivatives were computed. All of the GGA optimized structures had no negative Hessian eigenvalues; because hybrid DFT and MP2 optimizations were started from them, we expect them to be minima as well.

The DFT-D dispersion corrections were added by the external optimizer BOptimize with scaling factors as recommended by Grimme: 0.75 for PBE, 1.25 for BLYP, and 1.05 for B3LYP. For other functionals where Grimme's recommendations were not available, we used scaling factors as follows: 1.0 for MPBE, 1.25 for OLYP (like for BLYP), and 1.05 for BPBE (recommended for BP86, which is similar to BPBE). Finally, for the PBE1 hybrid functional, we used 0.75, the same scaling factor as for the pure GGA PBE. We have tried both single-point DFT-D calculations on geom-

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etries optimized with the same density functional, and reoptimization of geometries with the corrections applied. Because the latter did not bring significant changes in relative energies (a fraction of a kcal/mol only), we did not pursue reoptimizations any further, and all of the DFT-D energies were computed as single-point energy calculations.

The different methods that we employed (pure GGAs, hybrid DFTs, and MP2) produce frequencies of different quality. To obtain the thermal corrections required to calculate enthalpies, one usually scales down frequencies obtained for the hybrid DFs or MP2, while pure GGAs are known to systematically give lower frequencies than other methods. In the present study, we did not attempt to be very accurate in determining these enthalpy corrections, mainly because obtaining numerical second derivatives for hybrid DFs and MP2 is time-consuming with the codes we have used (Priroda and GAMESS-US). For most of the processes under scrutiny (isomerizations and polymer growth reactions), the effects of the thermal corrections on reaction enthalpies are likely to cancel out. Thus, for all MP2 and hybrid GGA calculations, we took enthalpy corrections from the corresponding PBE results. For DFT-D results, for GGA we took the corrections from the corresponding GGA DFT run.

For comparison, two other density functionals were included in our set of methods: the B97-D[29] functional by Grimme that is specially parametrized for use with DFT-D corrections, and the highly parametrized meta-GGA M06-L functional by Zhao and Truhlar.[50] For these functionals, we have used single-point calculations with the GAMESS-US code,[51] version Feb. 2009, on the RIMP2/L2 optimized geometries from the Priroda code. The L11 basis set with the same exponents and coefficients as those used in Priroda, but imported in the segmented contracted form native to GAMESS, was used for B97-D and M06-L computations (we note that due to differences in contraction scheme, total energies computed by GAMESS-US cannot be directly compared against Priroda results; the former have systematically lower total energies). Enthalpy corrections were always taken from the Priroda PBE/L11 results.

Finally, we have explored the performance of the C-Pot method by DiLabio, taking parameters for the carbon pseudopotentials from his work.[36] We have applied the PBE1 and B3LYP density functionals with the 6-31G+(d,p) basis set in single-point calculations on the Priroda MP2/L2 optimized geometries, using the Gaussian 03 program package.[52] Again, enthalpy corrections were taken from the Priroda PBE/L11 results.

Experimental heats of formations of hydrocarbons for calculation of the "experimental" reaction enthalpies used in this work were obtained from the NIST database.[53]

Results and Discussion

Polymerization Reactions. The quality of the modeling of normal alkanes has been the subject of numerous previous studies, some of which were concerned with iso- and homodesmotic reactions of their formation.[14,23,33,39,54,55] Schleyer introduced the term "proto-branching energy" for one of the sources of error in these calculations.[55] It refers to attractive 1,3 interactions between methylene groups that show up when one considers the formation of the normal hydrocarbon from C1 and C2 fragments. Because polymerization is similar in this respect, one large molecule assembles from the smaller units, such that new 1,3 and 1,4 interactions arise, dispersion interactions might be of importance for it as well.

We chose to consider enthalpies of addition (i.e., formal insertion of an alkene monomer into a terminal C−H bond of corresponding substrate) for four common alkene and alkadiene polymerization reactions. The reactions are shown in Scheme 1. There is only a limited number of experimental heats of formation for larger alkanes and alkenes available. Indeed, the determination of heats of formation for these species is a goal of several computational approaches, from Bensons' increment-based calculations[56] to semiempirical tight-binding methods[22,57] and parametrized group-equivalent approaches.[23] It is interesting in itself to see whether DFT-D methods are a viable alternative. Recent work[58] has shown that for a large number of hydrocarbons and small organic molecules the B3LYP method does not have a significant edge over the semiempirical PDDG/PM3 NDO method; tight-binding methods[22,57] also have shown reasonably good performance.

A direct comparison with the experiment is possible only in the case of ethene oligomers (for $n = 1$, 2, 3, and 6) and for the addition of a single propene into isobutane ($n = 1$, "syndio-"; this is the most stable conformer).[59] Therefore, we will compare our DFT and DFT-D calculations mainly to the MP2 results. We note that the MP2 method, especially in larger basis sets, is known to overestimate the dispersion energy. Parameterizations of the Moeller−Plesset method, such as scaled opposite spin (SCS)-MP2[60] and SCS-MP3,[61] MP2.5 (with scaled MP3 correlation energy contribution),[62] have been suggested to show better performance. However, in the present study, we use the nonparameterized, vanilla MP2 method (with its known, systematic errors) and compare the MP2 results with experimental data where available.

While comparing olefin monomer insertion energies computed with different functionals, we expect that, at least within the GGA family, we will have a similar quality of computed "intrinsic" energy differences, that is, of breaking of a monomer's C−C π-bond and formation of new C−C and C−H bonds in the corresponding insertion product. Thus, the differences in energies might be related to the quality of modeling of intramolecular nonbonding interactions. This assumption should be justified for the reactions in Scheme 1 (and Scheme 3 as well) because the molecules involved are not highly polar, nor do they possess a high degree of conjugation; as such, they are not problematic cases for GGA DFT.

The computed enthalpies are relegated to the Supporting Information, Tables S1 and S2. For the ethene and propene systems, the insertion enthalpies per monomer are similar (differ by a fraction of kcal/mol) for up to $n = 6$ (ethene) or 5 (propene) for all computational methods studied. Per-monomer enthalpies for the butadiene and isoprene systems are also similar for $n = 1$ and 2. Thus, to present our results
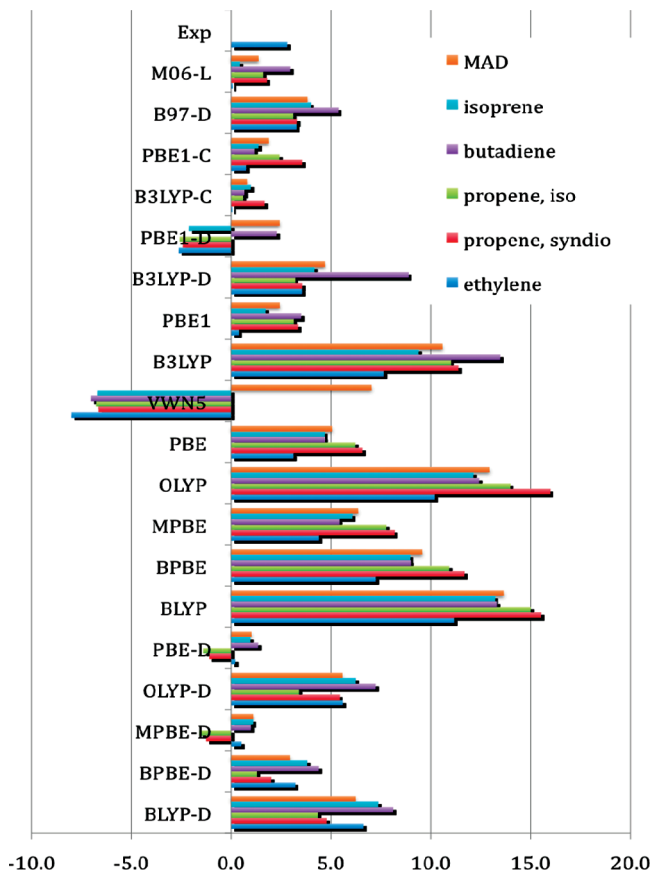
Figure 1. Differences between enthalpies of monomer insertion reactions (averaged per monomer; see the text) computed by density functionals and MP2, kcal/mol. For the ethene system, the experimental enthalpy difference with respect to the MP2 result is shown as well. MAD denotes the mean average deviation from MP2 over all polymer systems.

in a more compact form, we have averaged the per-monomer insertion energies for all calculated olefin insertion systems. The differences between DFT and MP2 computed enthalpies, averaged per monomer, are shown as a bar diagram in Figure 1. The mean average deviation from MP2 for different functionals over the polymer species studied is also shown (bars labeled as MAD). For the ethene system, the experimental difference from MP2 is plotted in Figure 1 as well (labeled exp.). MP2 overestimates the ethene monomer insertion enthalpy by −2.8 kcal/mol. The best agreement with experiment, within 1 kcal/mol, is shown by the BPBE-D, BLYP-D, unmodified PBE, and B97-D functionals. The worst performance is obtained with BLYP, OLYP (strong underestimation of the enthalpy), and with VWN5 (strong overestimation of it). Most of the unmodified density functionals underestimate the insertion enthalpy. MPBE-D, PBE-D, M06-L, unmodified PBE1, and two C-Pot-modified functionals, PBE1-C and B3LYP-C, yield ethene insertion enthalpies close to the MP2/L2 values.

There are no experimental heats of formation available for oligomers of our other model systems, propene, butadiene, and isoprene. Hence, we used the computed MP2/L2 results as "the truth" in these cases. One has to keep in mind, however, that the ethene MP2 results above show a tendency for overbinding, and thus the "best" results for monomer

insertion enthalpies should probably be the ones that underbind somewhat relative to MP2.

The isoprene and propene oligomers introduce branching, as compared to the polyethene. The influence of branching will also be studied in the section on alkane branching that follows, for test systems for which comparison with experiment is possible. Considering the polymerization model systems individually, we see that for propylene (both syndio- and isotactic) deviations from MP2 for uncorrected GGAs are higher than for ethene; the effect of the DFT-D correction was the largest for the propene system. Ethene and butadiene insertion that does not lead to a branched hydrocarbon product, and isoprene insertion in which the distance between the methyl side groups in the product is large, show somewhat lower sensitivity.

The VWN5 density functional systematically overestimates the monomer insertion enthalpies. All of the common GGA and hybrid density functionals underestimate the enthalpies, with errors particularly large in the cases of OLYP, BLYP, and B3LYP. Among the uncorrected DFT functionals, the hybrid PBE1 performs best. One can see that inclusion of the DFT-D correction to GGA DFT always decreases the errors. However, for OLYP-D and BLYP-D, they remain rather large. PBE-D and MPBE-D give results closest to the MP2 values. BPBE-D is slightly underbinding as compared to MP2, but, keeping in mind that MP2 itself is likely to somewhat overestimate the insertion enthalpies, we could say that this functional is probably one of the best. The corrected B3LYP-D functional still underestimates insertion exothermicities; for the PBE1-D, they are systematically overestimated, so that the MAD is similar to the uncorrected PBE1. Using the C-Pot pseudopotential method for B3LYP-C yields results very close to those of MP2/L2, with PBE1-C also having a small but slightly higher difference.

Alkane Branching and Insertion of Crowded Alkanes. The inability of most commonly used GGA and hybrid density functionals to accurately describe the relative stabilization of branched alkanes with respect to their linear isomers has received much attention.[12,17,29] For instance, experimentally the normal octane **1a** is less stable than 2,2,3,3-tetra-methyl-butane **1b** (Scheme 2), while GGA and hybrid density functionals predict the opposite. In the original DFT-D paper, Grimme[28] concluded that the dispersion correction (in its original parametrization) alone is not sufficient to result in the correct order of isomers **1a** and **1b**, for either the PBE or the BLYP functionals. On the basis of that, he concluded that not only "dispersion" is missing in density functional calculation but also a different effect that he named "medium-range correlation". The result was frequently cited afterward.[16,17]

In his latest revision of the DFT-D, Grimme tested his new B97-D functional including DFT-D terms and found that it indeed does predict the correct order of the octane isomers.[29] It is interesting to see what would Grimme's new DFT-D parametrization do for the case of octane branching with more common DFs like PBE or BLYP and their hybrids. In a recent paper, Cornimonbeauf and Schleyer[33] found that, in their version of the parametrization of the dispersion correction, this particular case (as well as other alkane
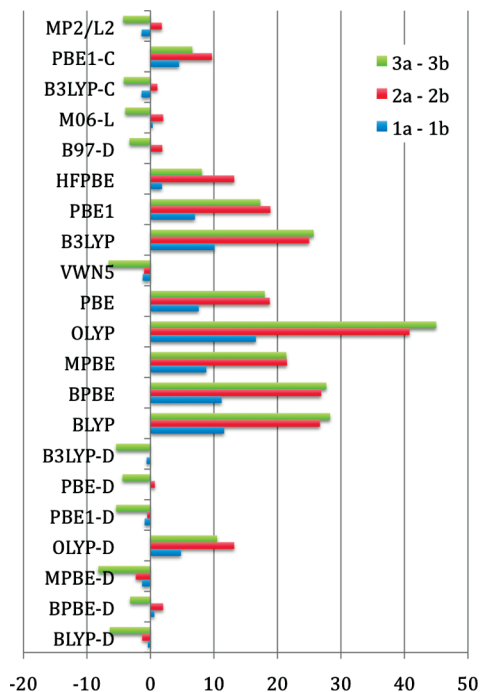
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Figure 2. Differences between experimental and calculated alkane branching enthalpies, kcal/mol.

Figure 3. Differences between experimental and calculated enthalpies of stepwise isobutene to methane insertion reactions, kcal/mol. The value *n* is the number of isobutene units to be inserted.

isomerizations) could indeed be described with dispersion-corrected PBE.

It is known that, while for small alkanes the branched isomers are the most stable, for larger alkanes effects of the sterical strain in the highly branched isomers can prevail over the branching stabilization, making linear or other less crowded alkane isomers more stable than the highly sterically crowded branched ones. To see if the DFT-D correction can predict the right trends for these cases as well, we included two isomers of tetradecane, **3a** and **3b** (Scheme 2), for which experimental heats of formation are known,[63] to our test set. The experimental paper contains data[63] for another alkane **2b** with a different branching pattern as well. Hence, we considered its isomerization from the linear tridecane **2a**, too.

We have also designed, on the basis of the availability of experimental heats of formation, another model system with stepwise increase of the sterical crowding (Scheme 3), the addition of isobutene to methane, yielding neopentane **4**, di-*t*Bu-methane **5**, and finally tris-*t*Bu-methane **2b**. This system has properties of both increased product branching and monomer insertion. Thus, it is analogous to the polyolefin model systems from the previous section of the paper. Because experimental enthalpies for its products are available, we can assess our methods, including MP2, directly against them. The resulting calculated enthalpies of the processes are shown in Figures 2 and 3 (as differences from the experimental values); the numbers are collected in Tables 1 and 2.

In agreement with literature data, common GGAs and hybrids (BLYP, BPBE, MPBE, OLYP, PBE, B3LYP, PBE1) yield the wrong order of isomers **1a** and **1b**, predicting the linear isomer **1a** to be the most stable. OLYP, BLYP, and B3LYP functionals have the largest errors, while for PBE-type functionals the errors are smaller. Only VWN5 and MP2
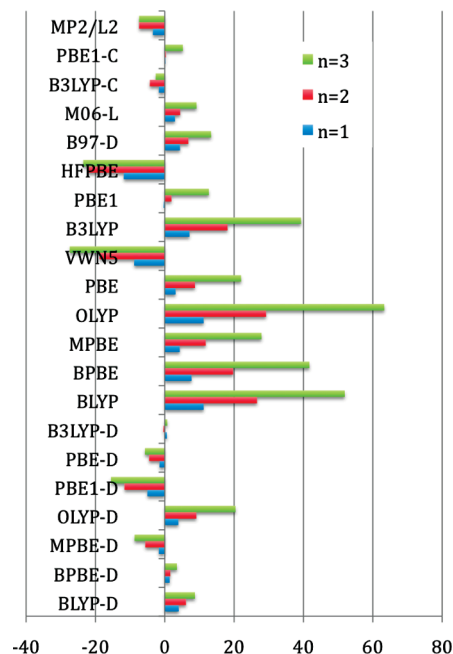
predicted the correct order (but see the discussion below on the B97-D and M06-L functionals). With the new version of Grimme's DFT-D correction, all GGAs except OLYP-D gave the correct order of the octane isomers, as did the corrected hybrids B3LYP-D and PBE1-D. Thus, with the "new" DFT-D parametrization, the energy order of the octane isomers **1a** and **2a** can be described even with standard, widely used functionals. Interestingly, an increase in the amount of exact exchange in the uncorrected PBE functional (from pure GGA to PBE1 with 25% to HFPBE with 100% of the exact exchange) decreased the error. The latter functional even predicted correctly the order of the octane isomers, although the error in it is still larger than for DFT-D corrected PBE.

For larger alkanes, application of the DFT-D correction leads to a significant decrease in the error as well. Again, the largest discrepancy among the corrected GGA functionals was found in the case of OLYP. However, for the tetradecanes **3a** and **3b**, most of the dispersion-corrected GGAs, as well as the MP2 method, overestimate the stability of the branched isomer.

The C-Pot corrected hybrid functionals, B3LYP-C and PBE1-C, also have significantly lower errors than the uncorrected ones. The B3LYP-C functional shows very good performance for alkane branching, similar to that of B3LYP-D; however, PBE1-C somewhat underestimates the enthalpies of the branched isomers and produces a qualitatively incorrect result for the octanes.

Figure 3 and Table 2 show the results for the methane crowding system of Scheme 3. Just like for the polymerization reactions, GGAs and hybrids strongly underestimate the exothermicity of the addition, while VWN5 strongly overestimates it. MP2 also overestimates insertion exothermicities, but not as bad as VWN5. Among uncorrected

Table 1. Calculated Alkane Branching Enthalpies, Shown as Differences from the Experimental Enthalpies, kcal/mol[a]

	BLYP	BPBE	MPBE	OLYP	PBE	VWN5	B3LYP	PBE1	HFPBE	B97-D	M06-L	MP2/L2	exp.
1a → 1b	11.6	11.2	8.8	16.6	7.6	−1.2	10.1	7.0	1.8		0.3	−1.4	−4.2
	−0.4	*0.6*	*−1.3*	*4.8*	*0.0*		*−0.6*	*−0.9*		*0.0*			
							<u>−1.4</u>	<u>4.5</u>					
2a → 2b	26.7	26.9	21.5	40.8	18.8	−1.0	25.0	18.9	13.2		2.0	1.8	18.3
	−1.3	*2.0*	*−2.3*	*13.2*	*0.7*		*−0.1*	*0.5*		*1.9*			
							<u>1.1</u>	<u>9.7</u>					
3a → 3b	28.3	27.7	21.4	45.0	18.0	−6.6	25.7	17.3	8.1		−4.0	−4.3	20.0
	−6.4	*−3.2*	*−8.2*	*10.5*	*−4.4*		*−5.4*	*−5.4*		*−3.3*			
							<u>−4.2</u>	<u>6.6</u>					

[a] Enthalpies with DFT-D correction applied are shown in italics; the ones obtained with the C-Pot method in the 6-31+G(d,p) basis are underlined.

Table 2. Calculated Methane *t*-Bu Saturation Enthalpies for *n* Isobutene Reagents, Shown as Differences from the Experimental Enthalpies, kcal/mol (See Scheme 3 for Description)[a]

n	BLYP	BPBE	MPBE	OLYP	PBE	VWN5	B3LYP	PBE1	HFPBE	B97-D	M06-L	MP2/L2	exp.
1	11.2	7.7	4.3	11.2	3.1	−8.8	7.1	−0.3	−11.8		2.9	−3.4	−18.0
	4.0	*1.4*	*−1.7*	*3.9*	*−1.5*		*0.6*	*−5.0*		*4.4*			
							<u>−1.7</u>	<u>0.2</u>					
2	26.6	19.7	11.8	29.2	8.7	−18.8	18.1	1.9	−22.1		4.4	−7.4	−31.2
	6.1	*1.6*	*−5.6*	*9.1*	*−4.5*		*−0.4*	*−11.6*		*6.8*			
							<u>−4.3</u>	<u>0.3</u>					
3	51.9	41.7	27.9	63.3	22.0	−27.4	39.3	12.7	−23.5		9.1	−7.4	−25.4
	8.7	*3.5*	*−8.7*	*20.4*	*−5.7*		*0.7*	*−15.5*		*13.4*			
							<u>−2.6</u>	<u>5.2</u>					

[a] Enthalpies with DFT-D correction applied are shown in italics; the ones obtained with the C-Pot method in the 6-31+G(d,p) basis are underlined.

functionals, the largest error is shown by OLYP, followed by the BLYP and B3LYP functionals, while PBE-like functionals perform better. HFPBE shows strong overestimation, due to the obvious importance of a description of changes of the exchange-correlation energy during the reaction, for which pure Hartree−Fock exchange is inadequate. The PBE1 hybrid was the best one among the uncorrected density functionals.

Applying the dispersion correction improves the agreement with experiment, with the best performance shown by BPBE-D. PBE-D and MPBE-D overcorrect; for OLYP-D the correction is not sufficient, although it improves the results. Among the hybrids, B3LYP-D performs very well with errors under 1.0 kcal/mol. PBE1-D yields significantly overestimated exothermicities. C-Pot corrected B3LYP-C shows good performance with some overbinding, while PBE1-C somewhat underestimates the exothermicity.

We have also tested another definition of the damping function for the DFT-D method, with Head-Gordon's power-twelve function.[40] In Table S3, we provide results for the functionals that performed best for DFT-D, BPBE and PBE, with corrections using eq 3, and no DFT-D correction at all, for the alkane branching (Scheme 2) and methane crowding (Scheme 3) test systems. One can see that usage of Head-Gordon's power twelve damping function leads to under-correction; although it reduces the errors of GGA DFs, they are still much larger that those obtained with Grimme's exponential damping function. The reason is that the power twelve function turns on too soon, as compared to the much steeper, exponential form of eq 3.

Potential Energy Surfaces. Scans of the intermolecular potential energy surface (PES) are usually performed around minima on the PES. Yang et al.[27] have studied the repulsive part of the methane dimer interaction curve and found that various density functionals differ significantly in that respect. They showed Becke88 exchange to be more repulsive than PBE exchange, and BLYP is more repulsive than PBE; all of these functionals are more repulsive than CCSD(T). Very recently, Becke published another study that considered interaction curves of noble gas dimers.[21] Similar observations were made for common exchange and correlation density functionals.

To rationalize our results described above, we performed potential energy scans for the collision of methane with neopentane (along the line of a C−C bond of the neopentane molecule, from the side of the latter's three methyl groups). For DFT and MP2 methods, we did fully relaxed PES scans, gradually decreasing the constrained carbon−carbon distance from 6 to 2 Å.

Figure 4 shows the energy differences between the MP2 potential energy scan curve and the curves given by other methods. The VWN5 functional consistently overbinds, as compared to MP2. This is a well-known property of the local density approximation functional.[64] The most "repulsive" density functional among those studied is OLYP, followed by BLYP and B3LYP. The PBE-containing functionals PBE, PBE1, and HFPBE give the closest resemblance to MP2 among the uncorrected functionals. The DFT-D correction plays a significant role, decreasing the repulsive character of the density functional. DFT-D for PBE makes it slightly overbind as compared to MP2. Interestingly, after addition of C-Pot pseudopotentials, the potential energy curves of PBE1-C and B3LYP-C became very close to each other; that is, with C-Pot B3LYP gets less repulsive but PBE1 gets more repulsive as compared to the uncorrected functionals.
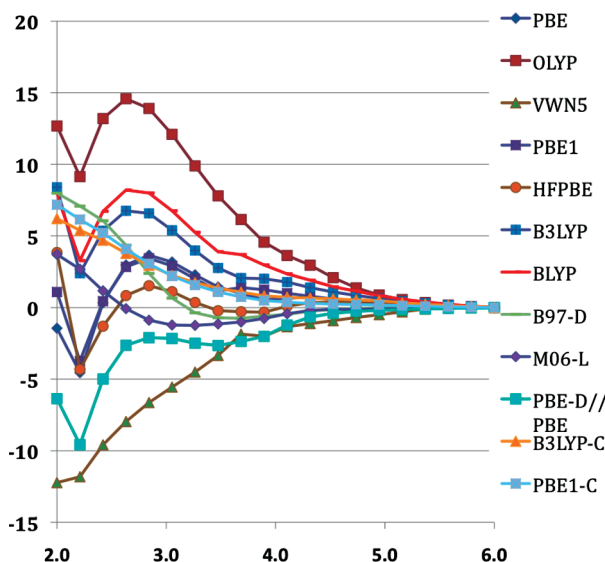
Figure 4. Relaxed PES scans for neopentane−methane interactions, energies relative to MP2, kcal/mol. The energies at a C−C distance of 6.0 Å were taken as zero for each method (distance in Å).

The character of repulsiveness of the density functionals parallels their performance for polymer growth and alkane branching systems described above. The most repulsive OLYP functional gives the larger errors; Becke and LYP containing functionals are over-repulsive as well, while PBE-D gives good but slightly overbound results.

The role and character of the intramolecular interations in alkanes were subject to a prolonged discussion in the literature. Originally, Pfitzer and Catalano[65] attributed the factors that describe alkane stabilities to electron correlation (dispersion) that leads to attractive 1,4 interactions in alkanes. Their reasoning was based on an incremental calculation scheme for the heats of formation. Gronert attributed the stabilities of alkanes, alkyl radicals, and alkenes to 1,3 repulsive interactions, again based on an incremental scheme.[66] Schleyer et al.[55] as well as others[67] discussed the stabilization due to the "protobranching" effect, that is, 1,3 attractive interactions in hydrocarbons. In a very recent paper by Rogers et al.,[68] another model was proposed that was able to describe hydrocarbon stabilities by a scheme that does not include any interactions as its terms, but counts only increments for hydrocarbons' hydrogens, of eight types depending on their chemical environment. The authors of the latter work point out that a model that fits the experimental data is not necessarily a proof of the reality of the "effects" it is based upon. In 2008, Estrada,[69] based on his topological model and semiempirical tight-binding calculations, showed that the ratio of 1,3 interactions to the total of all 1,2, 1,3, 1,4 interactions determines the relative stabilities of alkane isomers. His conclusions support Schleyers view of stabilizing 1,3 protobranching interactions; also, he has shown the importance of taking into account changes in the carbon nature due to its environment, which is absent in the "1,3 repulsion" model of Gronert.

Computationally, we can see from our and others' potential energy scans for alkanes and noble gases that the problem of most common DFT methods is overestimation of repulsive

interactions (or underestimation of attractive ones) at medium-range distances. The accuracy of the treatment of the interactions at these distances is crucial because it includes the 1,3 and 1,4 interactions that play an important role in hydrocarbons, as discussed above. As we have shown above, with a proper parametrization, the DFT-D approach is sufficient to make at least some of the commonly used GGA and hybrid functionals quantitatively accurate, that is, give the correct order of energies of branched and linear alkanes and the olefin monomer insertion enthalpies. It seems that the alternative approach of modifying pseudopotentials (the C-Pot method) works equally well, at least for some parametrizations (B3LYP-C). If we decompose the DFT-D energy corrections for our test molecules into H−H, C−C, and C−H components, we can see that the latter are largest in magnitude and contribute most to the DFT-D energy differences for the alkane branching and methane crowding tests (summarized in Table S4 of the Supporting Information). In the alternative C-Pot approach, only pseudopotentials for carbon are introduced; however, it somehow still works, at least for the B3LYP-C case, even for our hydrogen-rich test molecules from Schemes 1−3.

Performance of the "Dispersion-Aware" Functionals B97-D and M06-L. The B97-D functional was parametrized together with the DFT-D correction by Grimme.[29] Thus, it could avoid potential problems with overbinding due to dispersion being present both in the correction and in the density functional. The M06-L functional by Zhao and Truhlar is one of the highly parametrized meta-GGA functionals developed by their group, and one that is specifically recommended for main group compounds[50] (other variants of M06 family functionals exist, with different amounts of the exact exchange; we chose the semilocal M06-L functional for the performance reasons). In this study, we will apply these two specialized density functionals to the set of problems studied above. To save computational time, we took MP2 optimized geometries from Priroda calculations and computed single-point M06-L and B97-D energies for them. For the PES scans, MP2-optimized geometries of the points along the scans were taken as well.

The PES scans (Figure 4) show that both of these functionals perform well at intermediate distances; their energies are closer to the MP2 ones than those of the uncorrected GGAs and hybrids. They do not overbind as much as PBE-D does. Also, for intermediate distances they do not differ significantly from each other. However, at short ranges, B97-D rapidly becomes repulsive (reaching values closer to BLYP than to MP2), while M06-L remains "softer".

For the polyolefin growth reactions studied (as shown in Figure 1), M06-L shows results closer to those of BPBE-D (between it and MPBE-D); B97-D results are a bit farther from the latter, falling between BPBE-D and BLYP-D. Considering that MP2 is likely to have some overbinding, the performance of the "harder" B97-D for these systems might in fact be good.

For the alkane branching processes (Scheme 2), these functionals behave as follows. Both M06-L and B97-D predict the correct sign of the **1a**, **1b** energy difference (preference for the branched octane) and very small absolute

Table 3. Calculated MP2/L2 Energies of $C_{12}H_{12}$ Hydrocarbon Isomerizations, and Differences between MP2 and DFT Enthalpies, kcal/mol[a]

reaction	BLYP	BPBE	MPBE	OLYP	PBE	VWN5	B3LYP	PBE1	B97-D	M06-L	MP2/L2	exp.
6a → 6b	−2.5	−2.6	−1.9	−4.4	−1.6	0.4	−2.4	−1.9		0.1	−6.5	−7.0
	0.6	*0.1*	*0.7*	*−1.4*	*0.3*		*0.3*	*0.1*	*0.0*			
							<u>−0.4</u>	<u>−0.4</u>				
6c → 6a	−35.2	−5.6	−5.2	−4.2	−3.4	13.3	−24.2	8.6		−12.0	−36.3	
	−30.5	*−1.6*	*−1.5*	*0.4*	*−0.6*		*−20.3*	*11.3*	*−29.4*			
							<u>3.2</u>	<u>−4.1</u>				
6c → 6d	−30.8	−7.8	−7.4	−6.6	−5.9	7.6	−21.5	4.1		−7.0	40.2	
	−28.1	*−5.5*	*−5.3*	*−4.1*	*−4.3*		*−19.4*	*5.5*	*−26.5*			
							<u>2.7</u>	<u>−5.8</u>				
6c → 6e	−38.9	−10.1	−9.2	−10.1	−6.9	12.9	−26.6	6.1		−9.9	27.9	
	−34.2	*−6.1*	*−5.4*	*−5.5*	*−4.2*		*−22.7*	*8.7*	*−32.9*			
							<u>4.5</u>	<u>−4.7</u>				

[a] Enthalpies with DFT-D correction applied are shown in italics; the ones obtained with the C-Pot method in the 6-31+G(d,p) basis are underlined.

errors. The agreement for the *n*-tetradecane **3a** to the branched isomer **3b** energy is better than for most of the common DFT-D functionals (PBE-D, BLYP-D, MPBE-D, and B3LYP-D), but still shows some overestimation of the stability of the branched isomer.

For the stepwise isobutene to methane insertions leading to **2b**, which have increasing steric crowding (Scheme 3), both functionals give small errors that increase with increasing branching; for M06-L the error is slightly smaller than that for B97-D. Although the discrepancies with experiment for these two functionals are larger than for the best "standard" functional (BPBE-D), both of the specialized functionals avoid the overbinding due to the dispersion correction that PBE-D and MPBE-D demonstrate (Figure 3).

Hydrocarbon Isomerization and Cyclization Reactions. Recently, a caged $C_{12}H_{12}$ compound **6c** (Scheme 4) containing two cyclopropane moieties linked by aliphatic bridges, named as $[D_{3d}]$-octahedrane by its creators, has been synthesized. It was crowned by its creators as "the most stable $(CH)_{12}$ hydrocarbon".[70] However, subsequent studies[14,17] have shown that quite large discrepancies exist between relative energies of compound **6c** and other $(CH)_{12}$ isomers computed by density functional methods (such as B3LYP) and MP2. This system thus appears to be an interesting test case. We will apply our set of functionals with and without DFT-D corrections, and also perform MP2 calculations with a more reliable basis and with full optimization of geometries, on selected $C_{12}H_{12}$ isomers (Scheme 4). There are experimental heats of formation[53] for the dimethyl-naphthalenes **6a** and **6b**, which also happen to be isomers of $C_{12}H_{12}$. We then consider several structures for which computations were previously reported: the compound **6c**, a "good", low-lying isomer **6d** (compound **31** from ref 17) and a randomly chosen other isomer **6e** (compound **21** from ref 17).

Calculated isomerization energies between these $C_{12}H_{12}$ hydrocarbons are presented in Table 3. First, we note that compound **6c**, according to any of the pure local, GGA, hybrid DFT, and MP2 results, is less stable than either of the dimethyl-naphthalenes. To our knowledge, there is no experimental heat of formation of the octahedrane published. The previously published CCSD(T)/cc-pVDZ//MP2 value by Schreiner et al. for the energy of the reaction **6c** to **6d** is +25 kcal/mol;[17] however, the basis set used is fairly small.

One of the most recent higher-level results is a complete basis set extrapolated CCSD(T) result by Csonka et al., of +20.5 kcal/mol.[71] Comparison of these values to our MP2/ L2 energy of +30.4 kcal/mol shows that, probably, our MP2 energy is slightly too high.

Second, for the isomerization of the naphthalene isomer **6a** to **6b**, inclusion of the DFT-D correction improves the DFT (both pure GGA and hybrid) results, as compared to the experimental value (−7 kcal/mol, from the NIST database[53]). Both M06-L and B97-D functionals yield perfect agreement with experiment. The local density approximation yields the smallest error as compared to uncorrected GGA functionals, but with the opposite sign, which is typical, as we have seen above. This points to the importance of the inclusion of dispersion for the treatment of interacting CH_3 groups.

The influence of the DFT-D corrections on the results of other reactions is also beneficial (as it decreases the differences with MP2) but rather small. For the C-Pot methods, B3LYP-C and PBE1-C, the discrepancies also become smaller than for the uncorrected hybrid functionals.

Third, and most interesting, there is a very pronounced difference between the results from the BLYP and B3LYP density functionals, on one hand, and all other methods, on the other, for isomerization energies involving compound **6c**. Both BLYP-containing methods strongly underestimate its stability relative to the naphthalenes and compounds **6d**, **6e**. The failure of BLYP and B3LYP was already reported by Schreiner et al.[17] Here, we note that it cannot be ascribed to either the Becke-88 exchange or the Lee−Yang−Parr correlation functionals alone, because other combinations we have considered that contain either of them (BPBE and OLYP) yield results that are in agreement with other GGA methods and are close to the MP2 values. The result also cannot be ascribed to the Becke88 + LYP functional being too repulsive, because the OLYP functional that is the most repulsive functional studied (see the PES discussion above) does not have such large errors as BLYP.

Inclusion of the exact exchange in B3LYP shifts the results in the right direction, but these results are still very far from the correct ones. For the PBE functional, inclusion of exact exchange (PBE1) makes the results worse, overstabilizing compound **6c**. It seems that, for the molecule **6c** in case of

Table 4. Enthalpies of Reactions for C_3H_6 and $C_{10}H_{16}$ Hydrocarbons, Shown as Differences from the Experimental Enthalpies, kcal/mol (See Scheme 5 for the Description)[a]

reaction	BLYP	BPBE	MPBE	OLYP	PBE	VWN5	B3LYP	PBE1	HFPBE	B97-D	M06-L	MP2/L2	exp.
7a → 7b	−4.6	−0.8	0.1	−3.0	1.1	9.5	−0.6	5.2	17.4		−0.7	4.1	25.3
	−1.6	*1.7*	*2.4*	*0.0*	*2.8*		*1.9*	*6.8*		*−1.9*			
							6.3	5.4					
7a → 7c	−11.2	−5.9	−4.3	−9.4	−3.0	7.5	−5.7	2.9	21.3		−7.8	5.4	36.6
	−4.8	*−0.3*	*0.9*	*−2.9*	*0.9*		*−0.2*	*6.8*		*−6.8*			
							6.7	1.1					
7a → 7d	−20.1	−11.3	−9.2	−15.6	−7.4	7.1	−12.2	1.1	27.2		−10.7	2.3	26.2
	−10.8	*−3.2*	*−1.6*	*−6.2*	*−1.7*		*−4.1*	*6.8*		*−12.1*			
							3.2	−1.5					
7a → 7e	−11.8	−10.7	−8.3	−17.1	−6.5	6.6	−6.5	−0.8	18.1		−15.3	2.4	75.0
	−4.3	*−4.2*	*−2.2*	*−9.4*	*−2.0*		*0.0*	*3.7*		*−9.6*			
							8.9	−1.0					
n-C$_3$H$_6$ → **8**	7.6	2.6	2.6	2.4	2.2	−0.8	5.8	−3.5	0.6		−2.9	1.3	7.9
	5.0	*0.2*	*0.0*	*0.0*	*−0.1*		*5.4*	*0.3*		*2.1*			
							−0.1	−1.5					

[a] Enthalpies with DFT-D correction applied are shown in italics; the ones obtained with the C-Pot method in the 6-31+G(d,p) basis are underlined.

the combination of the Becke88 and Lee−Yang−Parr functionals, some error cancellation, which exists for other functionals, does not work.

The [D_{3d}]-octahedrane test is also the case where B97-D and M06-L give dissimilar results (Table 3). The enthalpies of the processes involving the octahedrane calculated by M06-L are closer to the ones given by most of the GGA functionals (BPBE, MPBE, etc.). At the same time, B97-D shows very large differences, placing it next to the BLYP and B3LYP density functionals.

While application of the DFT-D correction to all of the reactions in Scheme 4 (Table 3) somewhat improves agreement between the DFT and MP2 results for all GGAs and B3LYP (but not for PBE1), it cannot completely fix the performance of BLYP and B3LYP. One would think that the failure of the two latter functionals might have nothing to do with the over-repulsiveness of these DFs that is corrected by DFT-D. However, the C-Pot method B3LYP-C decreases the differences between MP2 and B3LYP quite dramatically. Combining C-Pot with PBE1 (to give PBE1-C) changes the energy difference in the opposite direction as compared to PBE1-D.

These observations require some rationalization. Molecule **6c** is a polycyclic molecule; besides that, some of its cycles are three-membered cyclopropane rings that are known to be chemically different from alkanes and alkenes. Either property might lead to the failure of the BLYP combination. Previously, poor performance of B3LYP was reported for terpene cyclizations and isomerization reactions by Matsuda and co-workers.[18]

Thus, we have added isomerization reactions of selected $C_{10}H_{16}$ hydrocarbons for which experimental heats of formation are available: terpenes (camphene and 3-carene), adamantane, pentamethyl-cyclopentadiene, and methyl-dicyclopropyl-cyclopropane (Scheme 5). Also, we have calculated the simple propene to cyclopropane cyclization reactions with all our methods. (We note that, for the smaller carbocycles, the experimental values have some discrepancies. There are two heats of formation for cyclopropane on the NIST website, leading to either 4.5 or 7.9 kcal/mol for the

experimental cyclization enthalpy; we took the latter value to be "correct".)

Results are assembled in Table 4. With respect to the propene to cyclopropane cyclization, BLYP and B3LYP show a difference, predicting a higher endothermicity of the reaction as compared to the other density functionals and MP2; M06-L and PBE1 overestimate the stability of cyclopropane. An underestimation of cyclization enthalpies by B3LYP was noted previously in the work by Matsuda.[18] OLYP, being more repulsive than BLYP according to our PES scans, does not underestimate the stability of cyclopropane as strongly and neither does BPBE. The picture is similar to that observed for the octahedrane; however, while differences of Becke + LYP methods per cyclopropene ring are clearly present, they are unlikely to be responsible for all of the discrepancies of the octahedrane, which are much larger that just twice the difference of cyclopropane enthalpy.

Studying the isomerizations of one of the $C_{10}H_{16}$ isomers, adamantane **7a**, to various other isomers (caged molecule, the camphene **7b**, a molecule rich with terminal methyl groups **7d**, and hydrocarbons containing cyclopropane fragments, the 3-carene **7c** and **7e**; see Scheme 5) also allows us to probe the importance of the dispersion interactions and the peculiarities of hydrocarbons with cages and small rings. The results are collected in Table 4. The general picture for the common DFs is as usual; DFT-D improves the energies for all of them, except for PBE1, which is the best among uncorrected functionals. The C-Pot method usually has somewhat larger errors in case of B3LYP-C but smaller ones for PBE1-C.

For the isomerization of adamantane to pentamethyl-cyclopentadiene **7d**, which has numerous 1,4 interactions between its five methyl groups, PBE-D, MPBE-D, and PBE1 perform best, while errors for the "repulsive" BLYP and OLYP functionals are large and cannot be fixed entirely by the dispersion correction. As in the previous similar cases, B3LYP-D performs significantly better than the uncorrected B3LYP, while errors for PBE1, which already had a good performance by itself, are increased by the DFT-D approach.
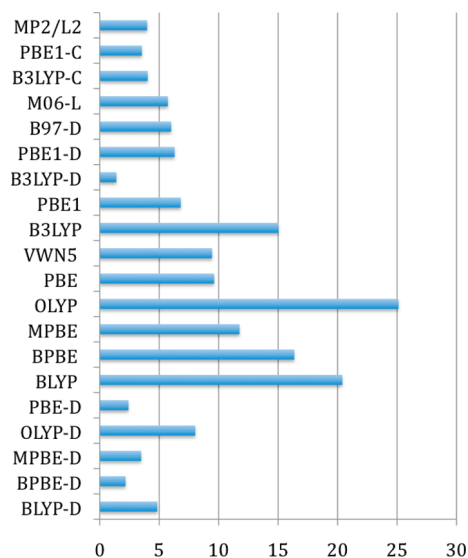
Figure 5. Mean absolute deviations between computed and experimental enthalpies for the set of isomerization reactions from Schemes 2, 3, and 5, in kcal/mol.

The C-Pot corrected PBE1-C and B3LYP-C methods both show better agreement with the experiment.

M06-L and B97-D show fairly large differences with the experiment for reactions **7a** to **7c−e**, overestimating stabilities of the latter with respect to adamantane. For the oligocyclopropane **7e**, the discrepancy for M06-L is the largest; for pentamethyl-cyclopentadiene **7d**, both functionals overestimate its stability by over 10 kcal/mol. We note that MP2 shows a rather good performance, as compared to experiment, and that most of the functionals we used, in their DFT-D corrected form, also performed well.

Thus, it seems that the large deviation of the energy of molecule **6c** computed with BLYP, B3LYP, and B97-D as compared to other methods is really a failure of the former density functionals. We cannot trace this failure to the presence of any particular molecular fragment. Grimme's DFT-D corrections do not depend on the hybridization of the atoms; thus, one could possibly expect the R_0 and C_6 parameters for cyclopropane atoms to be slightly different from those of other types of carbon. However, this does not seem to be a problem for many of the other reactions that we have considered: the polymerization processes that involve C^{sp3} to C^{sp2} changes, and the isomerizations of $C_{10}H_{16}$ that contain many different types of the carbon atoms, including the cyclopropane ones. Thus, we feel that slight changes in the $C_6 R^{-6}$ parameters can be ruled out as being the problem.

To summarize our results, we made an average estimation of the performance of the methods used in this work. We have computed the mean absolute deviations (MAD) of the calculated enthalpies over two sets of isomerization reactions (those on Schemes 2 and 5) and one set of monomer insertions (Scheme 3) where experimental data are available. The MAD values are shown in Figure 5. The corrected functionals B3LYP-D, BPBE-D, and PBE-D possess the smallest MADs over these sets, lower than 2.5 kcal/mol. (Note, however, that the sets do not include the octahedrane case, where B3LYP-D has larger differences with MP2

method and other functionals.) This indicates the importance of the dispersion corrections. Most of the other functionals that include dispersion corrections in the form of DFT-D or C-Pot perform acceptably, with MADs under 5 kcal/mol. The exceptions are PBE1-D, which shows strong overattractiveness, and thus the MAD are not significantly lower than those of uncorrected PBE1, and OLYP-D, which is still over-repulsive despite the corrections. The specialized B97-D functional and the highly parametrized M06-L perform well for polymerization and alkane branching, but show larger errors for $C_{10}H_{16}$ hydrocarbon isomerizations; thus, their MADs are slightly over 5 kcal/mol. Among the uncorrected density functionals, PBE1 shows the best performance, and OLYP the worst.

Conclusions

We have systematically investigated the performance of DFT on several selected test cases, olefin polymerization thermodynamics, alkane branching, and isomerization of various cyclic/caged hydrocarbons such as $C_{12}H_{12}$ and $C_{10}H_{16}$. Our approach was to combine the DFT benchmarking of interesting systems where experiment is not available against MP2 methods, with a comparison of both MP2 and DFT results against experimental ones where the latter are available. This was done specifically for systems that were chosen to be analogous to our systems of interest.

The results show that commonly used GGA and hybrid functionals perform poorly in many cases: all of them strongly and systematically underestimate the enthalpies of olefin monomer insertions; the stabilities of branched alkanes and hydrocarbons with many 1,4 methyl−methyl contacts are also strongly underestimated by these methods.

The application of the DFT-D corrections as proposed by Grimme improves the results considerably for most of the functionals and model systems we have tested. The best qualitative agreement for our test cases can be obtained by using the BPBE-D and PBE-D GGA functionals and the hybrid B3LYP-D (although the latter has problems describing the highly caged compound **6c**). Among uncorrected density functionals, PBE1 has shown the best performance, while OLYP and BLYP were usually the worst.

Other approaches, like the heavily parametrized M06-L functional, the B97-D functional, and the parametrized pseudopotential C-Pot method, also in general perform reasonably well for the cases dominated by dispersion.

The performance of density functionals was analyzed by considering the repulsive part of the alkane−alkane potential energy surfaces. There is a similarity between the over-repulsive character of a density functional (the most repulsive being OLYP, the least being PBE) and its performance for olefin insertion and alkane branching enthalpies. The GGAs and hybrids that we have studied are over-repulsive as compared to MP2, and the local VWN5 is overattractive. The introduction of the DFT-D correction amends the over-repulsiveness of the density functional; PBE-D shows slight overattractiveness as compared to MP2. Thus, the DFT-D correction with the proper parametrization and choice of density functional is sufficient (despite previous reports[16])

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for a qualitative description of intramolecular nonbonding interactions within hydrocarbons.

In cases where application of the correction is not desirable, one might test for the importance of the dispersion interactions by using the least and the most repulsive functionals (PBE or PBE1 and OLYP, correspondingly).

Not every problem of DFT can be solved by the simple DFT-D correction. For the case of the caged compound **6c**, BLYP, B3LYP, and B97-D show large errors, which are not directly related to the repulsive character of the DFs, because the most repulsive functional (OLYP) does not have this problem. These errors cannot be corrected by DFT-D but, in the case of B3LYP-C, have been successfully fixed by the C-Pot approach.

Supporting Information Available: Tables with calculated enthalpies of polymer growth reactions, and their deviations used to create Figures 1; table with comparison of two damping functions; table with components of the DFT-D energy differences for the selected reactions; and table with selected results with the power-twelve damping function. This material is available free of charge via the Internet at http://pubs.acs.org.

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