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Interaction between *n*-Alkane Chains: Applicability of the Empirically Corrected Density Functional Theory for Van der Waals Complexes[†]

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Abstract: The geometries, interaction energies, and vibrational frequencies of a series of *n*-alkane dimers up to dodecane have been calculated using density functional theory (DFT) augmented with an empirical dispersion energy term (DFT−D). The results obtained from this method for ethane to hexane dimers are compared with those provided by the MP2 level of theory and the combined Gaussian-3 approach with CCSD(T) being the highest correlation method [G3(CCSD(T))]. Two types of dimer isomers have been studied. The most stable isomers have the two carbon chains in parallel planes, whereas the second ones have the two carbon chains in the same plane. Butane is found to be the shortest carbon chain to form dimers with similar properties, that is, a constant average distance between the monomer carbon skeletons, a similar increment per CH_2 unit for the dimer interaction energy, and comparable dimer symmetric stretching frequencies. The values and trends obtained from the DFT−D approach agree very well with those obtained from MP2 for the geometries and vibrational frequencies and from the G3(CCSD(T)) method for the energies, validating the use of DFT−D for the study of large hydrocarbon complexes.

1. Introduction

Despite some success in the description of short-range weak interactions,[1,2] application of usual density functional theory (DFT) to van der Waals complexes is not theoretically justified and gives generally erroneous results in many systems involving nonbonding interactions.[3−7] The incapacity of most of the present exchange-correlation functionals based on the local density approximation (LDA), generalized gradient-corrected approximations (GGA), or more sophisticated meta-GGA to treat properly long-range interactions is now recognized. Therefore, significant progress in making DFT more appropriate for weakly interacting systems has been made in recent years. Long-range density functional theory, applying to nonoverlapping[8−10] and also overlapping electron densities,[7,11] has been proposed and applied to rare-gas dimers and rare-gas atoms interacting with small molecules[9,10] and arene dimers[12] and to more extended systems.[13,14] van der Waals interaction energies of small dimer systems have also been calculated using the symmetry-adapted perturbation theory and the time-dependent DFT method.[15,16] Molecular polarizabilities, from which dispersion interaction energy can be calculated, have been estimated from time-dependent calculations[17] or from the instantaneous dipole moment of the exchange hole.[18−20] New combinations and parametrizations of GGA[21,22] or meta-GGA[23] exchange-correlation functionals have also been proposed to allow the incorporation of the long-range part of electron correlation.

Dispersion effects are naturally accounted for in the wave function methods including a sufficiently high-level electron

correlation, but these methods are relevant only for small-size compounds and must be essentially used for benchmark calculations.

Because van der Waals interaction energies are important for large systems, Wu and Yang[24] have proposed an empirical dispersion energy correction (E_{disp}) to the usual DF energy (DFT−D approach), using atomic C_6 coefficients, derived from molecular C_6 coefficients. The idea of using a correction term originates from the works for correcting the Hartree−Fock (HF) method[25−27] and from Elstner et al.[28] for correcting the self-consistent-charge tight-binding method. Whereas the inherent nonlocal character of the Hartree−Fock method provides a correct description of the long-range exchange repulsion intermolecular forces, the DF approaches based on the local density expansion are not strictly applicable, and their performance depends on the particular exchange-correlation functional. The questions of the explicit form of damping functions that assures E_{disp} to be zero at the overlapped electron density region and one at the long distance were treated by Wu and Yang[24] and by Zimmerli et al.[29] Grimme has concluded that a proper scaling of E_{disp} is needed for each particular density functional.[30] Instead of scaling the empirical dispersion energy, Jurečka et al.[31] adopted a global scaling factor of the atomic van der Waals radii, optimized for a training set of noncovalent complexes. The transferability of this scheme was reported to be very satisfactory on the basis of the interaction energy values obtained for a set of small weak complexes and employing different LDA, GGA, and meta-GGA functionals. More recently, the inclusion of higher-order correction terms, involving C_8 and C_{10} coefficients associated with an adequate damping function, was proposed by Johnson and Becke,[20] aiming at a better description of π stacked systems. All the above-mentioned methods are tested on training sets including small-size weakly bound complexes, for comparison with high-level post-Hartree−Fock results.

The goal of this work is to verify the applicability of a computationally efficient technique with a good transferability and acceptable errors to structures and interaction energies of molecular complexes. Such a methodology is necessary for the study of systems involving alkane−alkane, alkane−water hydrophobic, and hydrogen-bonding interactions. Handling large scale systems with DFT methods augmented with a damped empirical dispersion correction (DFT−D) is generally performed with GGA functionals. Variational density fitting and the use of the auxiliary density in the exchange-correlation potential[32] calculation allows a substantial speedup. The results presented in this work concern dimers of saturated hydrocarbons.

For small dimers, the DFT−D results are compared with those obtained at the MP2 and the combined G3(CCSD(T)) levels of theory[33] employed to correct the interaction energies for the basis set and correlation limit errors. Results obtained with classical molecular mechanics (MM) are also used for comparison.

2. Methods

2.1. Dispersion Correction. The dispersion term, limited to the dipole−dipole contribution to the dispersion interaction
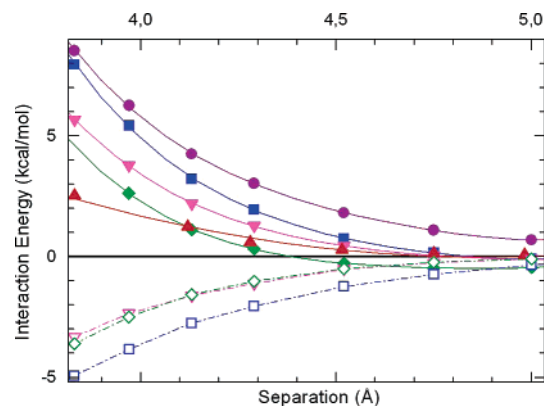

Figure 1. Interaction energy (IE) between two butane molecules in the butane dimer (isomer **a**) calculated using BLYP (●), revPBE-LYP (■), PBE (◆), and TPSS (▼) compared with the HF values (▲): (top) without their correlation interaction contribution and (bottom) correlation-only interaction energy for revPBE-LYP (□), PBE (◇), and TPSS (▽).

energy, $E_{disp} = -\sum_{i=1}^{N} \sum_{j=i+1}^{N-1} (C_6^{ij}/r_{ij}^6) f_{damp}(r_{ij})$ is expressed as the sum of all possible contributions of the i,j atom pair in an N-atomic system with an interatomic distance r_{ij}. In the DF approach including a damped empirical correction for the van der Waals interactions, E_{disp} is simply added to the usual DF energy and the ∇E_{disp} is added to the DF energy gradient. The present E_{disp} expression, limited to the first C_6/R^6 term, contains implicitly most of the physical intermolecular dispersion via the fitting of the atomic C_6 coefficients to molecular C_6 values, obtained from a training set of 44 pairs of molecules including hydrocarbons and other small organic compounds.[24]

The dispersion coefficients $C_6^{ij} = (2C^iC^j)/(C^i + C^j)$ are computed from the atomic C_6^i, as proposed by Wu and Yang,[24] but averaged over the possible hybridization states of the atoms, which are 2.845 and 26.360 au for H and C atoms, respectively. The damping function used is $f_{damp}(r_{ij}) = 1/(1 + e^{-\alpha(r_{ij}/r_0 - 1)})$ with $\alpha = 23.0$[24] and with r_0 being the sum of the atomic van der Waals radii.[34]

The dispersion correction energy, its gradient, and second derivative were implemented in the deMon2K program,[35] allowing geometry optimization and vibrational frequency analysis.

We used a nonscaled empirical dispersion term, unlike in previous DFT−D calculations[30,31] where different scaling factors were adopted depending on the chosen exchange-correlation functionals. In fact, scaling was used previously to correct the erroneous behavior of GGA exchange functionals, which either show an unexpected attractive tendency in the van der Waals region (and thus avoid a double counting of the "dispersion") or, in contrast, have a too strong repulsion slope in this region. The latter trend is mainly displayed by the Becke exchange functional,[36] whereas PW91[37] and PBE[38] exchange functionals are responsible for the former.

2.2. Choice of the Exchange-Correlation Functionals. In order to illustrate the above-mentioned problem, we report in Figure 1 the repulsive (top) and correlation (bottom) contributions to the nondispersion-corrected interaction
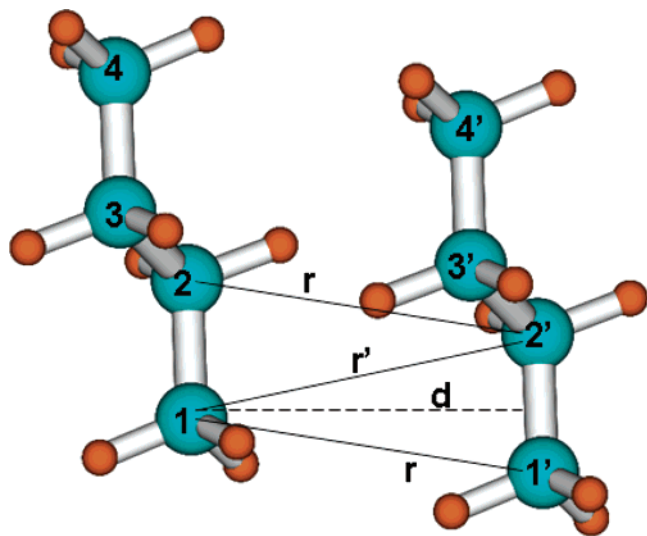
Figure 2. Geometric parameters *r*, *r′*, and *d*, defined using the butane dimer (isomer **a**).

energy between two butane molecules as a function of their shortest C···C intermolecular distance (*r′* in Figure 2). For proper comparison of the exchange functionals, the repulsive interaction energies have been calculated by removing the correlation contribution from the total interaction energy (without dispersion). The optimized butane monomer energies were used. These values are compared with the HF interaction energies (using the MP2-optimized structures). As shown in Figure 1 (top), the revised version of PBE, that is, revPBE,[39] and TPSS[40] repulsive curves are close to HF for the long distances, that is, between 4.4 and 5 Å, where they reach zero, ensuring no double counting of "dispersion" effects. In contrast, Becke (B) exchange leads to a much stronger repulsion, whereas PBE is attractive for distances beyond 4.4 Å. Similar conclusions have been reported for the benzene−benzene interaction.[14]

As expected, correlation interaction energies are more attractive with decreasing the separation between the butane monomers (Figure 1, bottom). The LYP[41] functional shows a larger correlation interaction than the other two functionals.

Using the PBE exchange and correlation functionals without empirical dispersion correction leads to a small minimum for the butane dimer (−0.8 kcal/mol at a separation of 4.5 Å). A PBE−D calculation leads thus to a much too large stabilization of 4.1 kcal/mol compared with the MP2 and CCSD(T) interaction energy of 2.7 kcal/mol.

As shown in Figure 1, combining the PBE correlation with the revPBE exchange yields a large repulsive interaction in the range of 4−4.4 Å which cannot be compensated by the damped dispersion correction. Combining the "semiempirical" revPBE exchange, adjusted on atomic exchange energies, with the LYP correlation functional, self-interaction (SI)-free by construction, allows a good balance of repulsive and attractive effects between the two subsystems. In fact, the revPBE exchange leads to less SI error than PBE (5 times less for the H atom). The PBE exchange SI error is mostly compensated by the SI error of the PBE correlation itself. Therefore, combining the revPBE exchange with the PBE correlation is much less appropriate than combining it with the LYP correlation.

The calculations reported further are thus obtained using the revPBE-LYP functionals, augmented with the damped empirical dispersion, as described above and which will be referred to as DFT−D.

Finally, the result that the TPSS repulsion curve is very comparable to the HF interaction energy curve validates the construction of an adequate meta-GGA correlation functional, in which dispersion effects could be incorporated, using a strategy adopted by Zhang and Salahub[23] and including alkane van der Waals complexes in the training set.

2.3. Computational Details. The Dunning correlation-consistent cc-pVTZ basis,[42] associated with automatically generated auxiliary basis functions up to *l* = 4 for fitting the density,[35] has been used for all dimers. For the DFT−D calculations, the exchange-correlation potential was computed using the variationally fitted density.[32]

The DFT−D results for smaller C_nH_{2n+2} dimers (*n* = 2−4, 6, and 8) were compared with the computations carried out with the Moller−Plesset second-order perturbation method (MP2) as implemented in the G03 code,[43] using the 6-31g-(d) basis set to optimize geometrical parameters and obtain vibrational properties. Single-point calculations at these geometries have then been performed to obtain energies at the cc-pVTZ level of theory (MP2/cc-pVTZ). It is a general consensus that the MP2 method combined with a relatively small basis set overestimates interaction energies in the van der Waals complexes. For this reason, the interaction energies between alkane moieties were also computed by the combined Gaussian-3 (G3) method:[33] a series of single-point energy calculations at the MP2/6-31g(d) optimized geometry were performed following the G3 algorithm. Instead of the usual QCISD(T) method suggested in the G3 approach, we have adopted the CCSD(T) calculations. These data are referred to as G3(CCSD(T)) in the text.

The obtained minima structures were localized by carrying out full geometrical optimization without imposing any constraint. The true minima on the potential energy surface (PES) for dimers up to octane were confirmed from the vibrational frequency analysis. The vibrational frequencies were obtained analytically with the G03 program and numerically with the deMon program. To minimize the numerical errors in the geometry optimization procedure, which are significant for weakly bound systems, the DFT−D calculations were performed using an adaptive grid with a tolerance equal to 10^{-14}. The tolerance of the energy gradients was equal to 10^{-5} to 10^{-6} hartree and for the energy convergences to 10^{-7} (DFT−D) and 10^{-8} hartree (MP2).

The amount of the basis set superposition error (BSSE) was examined following the counterpoise approach.

The MM results, reported for the series *n* = 2−12 of alkane dimers, have been obtained with the TINKER program,[44] using the OPLS-AA force field.[45]

3. Results

3.1. Geometries. As it is the case for long alkane chains in surfactants or in lipids, the *n*-alkane dimers with *n* ≥ 3 have been considered in a trans conformation. For these dimers, two types of isomers were found, as illustrated in Figure 3 for the octane dimer. The most stable complexes correspond
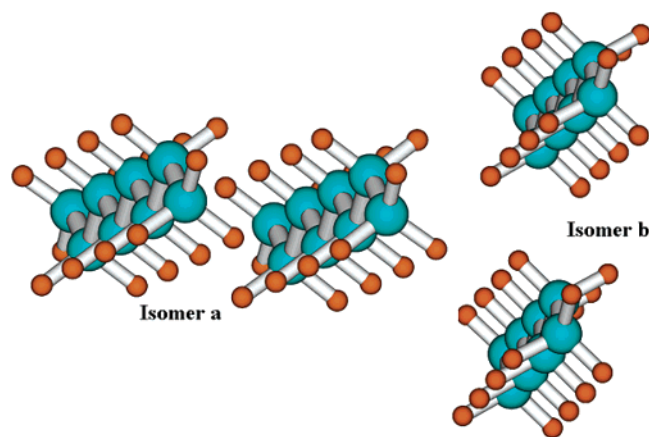
Figure 3. Schematic presentation of isomer **a** (the most stable minimum) and isomer **b** (the second minimum) structures of *n*-alkane dimers, using the results obtained for the octane dimer.

Table 1. Optimized Intermolecular Distances, r, r', and d (defined in Figure 2), between the Monomers of the C_nH_{2n+2} Dimers ($n = 1, 12$) Computed at the DFT$-$D/ cc-PVTZ Level[a]

n	2	3	4	5	6	7	8	10	12
r^b	4.10	4.18	4.20	4.21	4.21	4.22	4.22	4.23	4.23
	(4.22)	(4.23)	(4.24)	(4.23)	(4.22)		(4.22)		
r'^b	3.85	4.00	4.12	4.12	4.13	4.13	4.13	4.13	4.13
	(4.30)	(3.98)	(4.11)	(4.10)	(4.09)		(4.10)		
d^b	3.88	3.98	4.09	4.09	4.09	4.10	4.09	4.09	4.09
	(4.19)	(3.95)	(4.08)	(4.06)	(4.07)		(4.06)		
r^c		4.48	4.65	4.71	4.71	4.72	4.72	4.73	4.74
		(4.51)	(4.69)	(4.71)	(4.71)				
r'^c		3.95	4.04	4.07	4.09	4.09	4.10	4.11	4.12
		(4.04)	(4.09)	(4.09)	(4.10)				
d^c		3.94	3.95	3.95	3.96	3.96	3.96	3.95	3.95
		(4.02)	(3.98)	(3.96)	(3.96)				

[a] The values in parentheses are obtained from the MP2/6-31g(d) method for $n = 2-6$ and 8. [b] Most stable isomer **a** (Figure 3). [c] Second stable isomer **b** (Figure 3).

to two monomers with carbon skeletons in parallel planes (isomer **a**, Figure 3), whereas the less stable isomer **b** (Figure 3) is related to carbon skeletons in the same plane. For the ethane dimer, isomers **a** and **b** correspond to the same structure with the four carbons in one plane.

The geometries of the alkane dimers are defined by the intermolecular C···C distances illustrated in Figure 2 for the butane dimer, isomer **a**. These notations are valid for all alkane isomers. If the carbon atoms are labeled 1, 2, ...i, ...n for one monomer and $1'$, $2'$, ...i', ...n' for the second monomer, one finds n distances r, between the carbon pairs i and i' and $n - 1$ distances r', independently on the number n of carbons in the monomers. As an example, the butane dimer (Figure 2) has four equivalent r distances ($1-1'$, $2-2'$, $3-3'$, and $4-4'$) and three equivalent r' distances ($1-2'$, $2-3'$, and $3-4'$). It is clear from Figure 2 that the relative values of r and r' measure the translational shift of the carbon skeletons, in both isomers. The d parameter measures the distance between the parallel C$-$C bonds of the two monomers. All the r, r', and d values, presented in Table 1, have been obtained averaging the corresponding parameters

on the n calculated r and $n - 1$ calculated r' and d values for all dimers. The average values reported in Table 1 have a mean absolute error less than 0.02 Å for DFT$-$D and 0.05 Å for MP2. Moreover, all (i, i', $i' + 1$, $i + 1$) dihedral angles (see Figure 2 for illustration) are less than 1°. The propane dimers make an exception with average distances calculated with a mean absolute error of about 0.06 Å, whereas the two dihedral angles as mentioned above deviate from planarity by about 2$-$3° for MP2 and DFT$-$D.

The analysis of Table 1 reveals a very good agreement between the geometrical parameters obtained with the two different methodologies, especially for $n \geq 3$, allowing to draw general conclusions without referring to the method. The most stable isomers **a** with the C_n chains in parallel planes have r and r' values more similar than the other isomers **b** and, at the same time, a slightly larger distance d between the chains. Indeed, the $r - r'$ value amounts to about 0.1 Å for isomers **a** and 0.6 Å for isomers **b**, whereas the distance d between the alkane chains decreases by about 0.15 Å from the former to the latter. Finally, both isomers have comparable r' distances between the (i, $i' + 1$) carbon pairs. These results illustrate the fact that the shift of the monomers with respect to each other ($r - r'$) is correlated with the value of the distance d between the chains. Decreasing the electrostatic repulsion between dimer chains is achieved through both their relative shift and their larger separation. At the same time, shorter distances between the chains favor the dispersion attraction. Obviously, a shorter chain$-$chain distance in isomers **b** does not compensate the much longer r distance, yielding then a weaker dispersion attraction.

It is worth noting that the dimer chains from C_4 to C_{12} behave similarly, with a very nice invariability of the r, r', and d geometrical parameters. This allows us to anticipate that increasing a monomer chain by one CH_2 unit will increase by the same amount the electrostatic repulsion and the dispersion attraction for chains in parallel planes at about 4.10 Å and at about 3.95 Å in the same plane. The ethane dimer which contains only CH_3 groups and the propane dimer with two CH_2 against four CH_3 groups do not show the same characteristics as the longer alkane dimers, with shorter r, r', and d values. We can thus conclude that the butane dimer is the first "long" chain alkane dimer, with the same number of CH_2 as CH_3 groups.

Very recent MP2 calculations on n-alkane dimers up to decane, with D_2 fixed symmetry, have been reported, but their detailed geometries were not discussed.[46] Earlier MP2 studies on the potential energy surfaces of small hydrocarbon dimers (ethane and propane) reported a separation distance of 4.18 Å for the propane dimer.[47,48] In these works, C_{2v} symmetry was imposed, and the PES was described from the MP2 single-point interaction energies at various intermolecular distances fitted against a Morse potential. The separation distance between propane monomers found in ref 47 agrees well with the r values of 4.18 and 4.23 Å obtained at the DFT$-$D and MP2 levels, respectively, for the most stable isomer **a**, although a comparison between optimized structures and PES single points is not easy.

The OPLS-AA empirical potential calculations yielded r and r' values equal to 4.11 and 4.00 Å (isomer **a**), and 4.39

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Table 2. Calculated Interaction Energies (kcal/mol) of the Most Stable Structures of the Ethane, Propane, and Butane Dimers, Compared with Different Methods

	MP2[a] (this work)	G3[b] (CCSD(T)) (this work)	MP2[c] ref. 47	MP2[d] ref. 46	MP2[e] ref. 46	CCSD(T)[f] ref. 46	DFT−D[g] (this work)
C_2	−1.12	−1.00		−1.04	−1.35	−1.22	−1.28
C_3	−1.89	−1.86	−1.63	−1.64	−2.08	−1.87	−1.72
C_4	−2.58	−2.69		−2.44	−2.97	−2.74	−2.66

[a] MP2 opt 6-31g(d) basis; energy cc-pVTZ. [b] MP2 opt 6-31g(d) basis; CCSD(T) limit. [c] MP2 opt 6-311+G(d2f,2pd); geometry of monomers fixed. [d] MP2 opt 6-311G(dp); energy cc-pvTZ [e] MP2 opt 6-311G(dp); MP2 limit [f] MP2 opt 6-311g(dp); CCSD(T)limit. [g] revPBE-LYP-D opt cc-pvTZ.

and 3.75 Å (isomer **b**), respectively, for the considered series from $n = 3$ to 12. For the ethane dimer, the calculated r and r' values were 4.08 and 3.83 Å, respectively. These results are in relatively good agreement when compared with our DFT−D and MP2 calculations for the isomer **a**, despite an underestimation by 0.12 Å of the distance between the chains. In contrast, the distances found for isomers **b** are neatly underestimated with respect to the quantum chemical methods, with a distance between the chains too short by almost 0.3 Å. However, the relatively good agreement obtained for the largest interactions is encouraging for further use of this force field in combined DFT−D/MM approaches.

3.2. Interaction Energies. A dimer interaction energy (ΔE) has been computed as the difference between the energy of the dimer at the optimized geometry and the sum of the energies of the two monomers at infinity. The structures of the monomers have been fully optimized at all computational levels considered in this work, as described in section 2. Indeed, the BSSE correction has been evaluated for the ethane up to hexane dimers. For both MP2 and DFT−D calculations, its value decreases rapidly with increasing the number of CH_2's in the monomer and becomes already negligible for the butane dimer for MP2 and the propane dimer for DFT−D.

We have found it interesting to compare first, in detail, the DFT−D results with those obtained with post-Hartree−Fock methods, at different levels of theory for the ethane, propane, and butane dimers, separately. The "long" alkane dimers, including also the butane dimer, will then be discussed further.

3.2.1. C2 to C4 Dimers: DFT−D Compared with Post-Hartree−Fock Methods. The results obtained for the C_2, C_3, and C_4 dimers are compared in Table 2 for different methods. First, it is worth noting the overall good agreement between the various approaches, despite differences which are due to the respective approximations of the methods, and that we would like to comment upon.

The dependence of the MP2 electron correlation energy, for small hydrocarbon dimers, on the size of basis functions has been discussed previously[46,49] and shown to be less pronounced for the longer dimers.[46] The results reported for propane from ref 47 correspond to a dimer optimization with frozen monomer geometries.

The MP2 basis set limit calculations in ref 46 show a trend to overestimate the dimer stabilization with respect to the ethane to butane reported CCSD(T)(limit) values. The G3-(CCSD(T)) results in this work and the CCSD(T)(limit) from ref 46 show small differences which are probably due to slightly different geometries of the respective dimers and
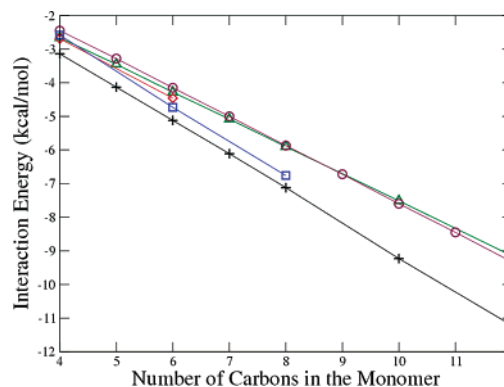

Figure 4. Interaction energy in kilocalories per mole of the isomers **a** of C_4 to C_{12} alkane dimers, computed with different methods. The symbols denote various computational approaches as follows: (△) DFT−D/cc-pvTZ, (○) MM−OPLS, (□) MP2/cc-PVTZ, and (◇) G3(CCSD(T)). The DFT−D dispersion interaction energies are denoted with crosses.

the different combined computations for the basis and correlation limits.

The values obtained from DFT−D are in very good agreement with those obtained from the CCSD(T)(limit) results. The evolution of the interaction energy from ethane to butane is also well-reproduced. In all methods, the dimer binding energy changes less from ethane to propane than from propane to butane, confirming that butane dimer can be considered as the first "long" alkane chain dimer.

Finally, let us mention that the isomers **b** of propane and butane dimers have evaluated interaction energies of −1.54 and −2.00 kcal/mol with DFT−D.

3.2.2. C4 to C12 Dimers: DFT−D Compared with MP2, CCSD(T), and MM Methods. A graphical comparison between the ΔE values obtained from the various methods is presented in Figure 4 for isomers **a** and Figure 5 for isomers **b**. The evolution of ΔE from C_4 to C_{12} chains shows a very regular linear dependency for both isomers and for all the methods. The same trend can be found from the MP2 interaction energies reported in ref 46 for C_4 to C_{10}. As already mentioned above, starting from butane, the $CH_2 \cdots CH_2$ interactions increase regularly going from C_n to C_{n+1} dimers.

The MP2 values for isomer **a** show a larger dimer stabilization of about 12% than revealed by the DFT−D interaction energies, with the same trend followed by the MP2 basis set limit calculations in ref 46 for the butane to decane series. However, the G3(CCSD(T)) corrections to the MP2 electron correlation in the case of the hexane dimer **a** yield $\Delta E = -4.46$ kcal/mol, agreeing well with the DFT−D
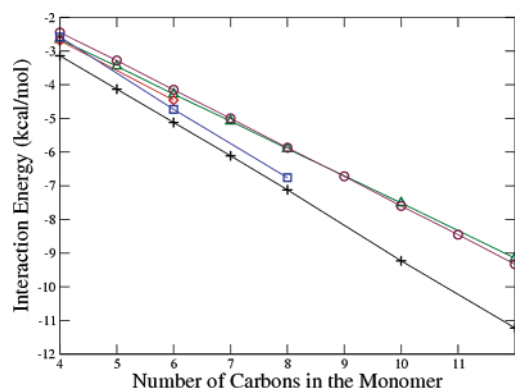
Figure 5. Interaction energy in kilocalories per mole of the isomers **b** of C_4 to C_{12} alkane dimers, computed with different methods. The symbols denote various computational approaches as follows: ($\triangle$) DFT−D/cc-pvTZ, ($\bigcirc$) MM−OPLS, ($\square$) MP2/cc-PVTZ, and ($\diamond$) G3(CCSD(T)). The DFT−D dispersion interaction energies are denoted with crosses.

value of −4.27 kcal/mol, whereas the MP2 value, at the same geometry, is −4.73 kcal/mol. The three methods yield very similar values for the stabilization of the hexane dimer isomer **b**.

It is interesting to note that the MM results are in very good agreement with the quantum mechanical values, especially for the most stable isomers **a**. This method obviously underestimates the energy difference between the two types of structures, that is, isomers **a** and **b**. This result is related with the underestimated MM intermolecular chain distances in isomer **b**, as shown in section 3.1.

For the most stable isomers, the average increase of interaction energy per CH_2 unit is estimated at −0.81 from DFT−D, −0.97 from MP2(limit),[46] and −0.86 kcal/mol from MM. From the G3(CCSD(T)) results for butane and hexane, a value of 0.88 kcal/mol can be proposed, which confirms the validity of the DFT−D description along with the chain lengthening. The average increase of interaction energy per CH_2 unit is much less for isomer **b**, since it amounts to −0.53 from DFT−D and −0.61 kcal/mol as deduced from the G3-(CCSD(T)) results for butane and hexane dimers **b**.

Since DFT−D geometries correlate well with those provided by MP2 methods which include implicitly the dispersion attraction, one can attempt to evaluate the dispersion increase along with the alkane chain lengthening, comparing the ΔE_{disp} and ΔE values provided by the DFT−D method.

The analysis of these values displayed in Figures 4 and 5 leads to the conclusion that attractive dispersion-like forces have a main contribution in alkane dimer formation. For the considered series of C_4 to C_{12} dimers, ΔE_{disp} is found to be somewhat larger than the total interaction energy. Interestingly, the difference between ΔE_{disp} and ΔE increases only from 0.14 to 0.70 kcal/mol for isomer **b** from C_4 to C_{12} dimers, whereas it changes from 0.48 to 2.07 kcal/mol for isomer **a**, showing that the repulsive electrostatic and electron exchange forces in the total interaction energies appear to have a larger effect for isomer **a** than for isomer **b**. At the same time, the dispersion interaction between the two alkane moieties is stronger in the case of dimers **a**. The two

monomers lying in mutually parallel planes (structure **a**) have $r(i, i')$ distances shorter by nearly 0.5 Å than those lying in the same plane (structure **b**), due to the stronger dispersion-like attraction. Therefore, higher ΔE_{disp} values obtained for isomers **a** correlate with closer contacts between carbon and hydrogen in this isomer in accordance with a conclusion drawn in ref 48 concerning the structure of the most stable minimum on the PES of the propane dimer. This conclusion is also confirmed by the average increase of "dispersion interaction" associated per CH_2 unit from butane to decane, which amounts to −1.0 for isomers **a** and −0.6 kcal/mol for isomers **b**.

The simultaneous increase of both attractive and repulsive intermolecular interactions with increasing the *n*-alkane size leads thus to a nearly linear relationship of the total interaction energy with *n*.

It is worth noting that dispersion energy also contributes to the total energies of the individual *n*-alkane monomers. This contribution varies from −3.7 for butane to −14.8 kcal/mol for dodecane, with a regular decrease of −1.4 kcal/mol per CH_2 unit. The internal E_{disp} value is thus about 50% larger than the dispersion contribution to the dimer binding. This shows that, in the alkane monomers, the damped dispersion at midrange contributes also to the total energies. However, the amount of stabilization provided by the internal dispersion in an alkane molecule is very small with respect to the other energy contributions (0.55% of the correlation energy for *n*-butane, 0.57% for isobutane, 0.70% for *n*-octane, and 0.81% for isooctane). This explains why this E_{disp} term cannot compete with some other effects, such as those governing the branched/linear alkane relative stabilities.[50]

The geometries and interaction energies obtained for *n*-alkane dimers show thus a very good agreement, when a comparison is possible, with the post-Hartree−Fock results. The performance of the revPBE-LYP-D method has also been verified for the two benzene dimers with sandwich (S) and parallel displaced (PD) structures for which the stabilization energy is due solely to dispersion interactions. Optimization of these dimers was performed at the revPBE-LYP-D/cc-pVTZ level and energies corrected for BSSE. The stabilization of the S dimer is 1.0 kcal/mol (distance 3.96 Å), whereas that of the PD dimer is 1.7 kcal/mol (distance 3.67 Å, displacement 0.95 Å). These values agree very well with CCSD(T) results reported with similar bases: 1.1 kcal/mol (S) and 2.0 kcal/mol (PD), with aug-cc-pVDZ,[51] and 0.7 kcal/mol (S) and 1.6 kcal/mol (PD), with cc-pVTZ.[52] The basis set extension effect on the above DFT−D values is comparable with that displayed by post-Hartree−Fock methods.

3.3. Vibrational Frequencies. Vibrational frequencies, within the harmonic approximation, have been computed at the DFT−D/cc-PVTZ and MP2/6-31g(d) levels of theory for a limited number of dimers, that is, ethane, propane, butane, hexane, and octane dimers (isomers **a**). Each dimer has six low-frequency modes. From the analysis of the six normal vectors, five of the low-frequency modes are assigned to coupled internal rotations of the CH_2 and CH_3 groups. Only one normal vector was found related with the stretching displacements of the *n* carbon atoms of one monomer with

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Table 3. Far-Infrared Intermolecular Stretching Vibrational Frequencies in cm^{-1} for the Most Stable Isomers **a** of C$_n$H$_{2n+2}$ Dimers (*n* = 2, 3, 4, 6, and 8) Computed at the DFT−D/cc-PVTZ and MP2/6-31 g(d) Levels

n	2	3	4	6	8
DFT−D	64.5 (sym)	53.9	59.3	58.9	57.9
	65.2 (asym)				
MP2	46.9 (sym)	51.3	53.9	58.3	56.1
	48.1 (asym)				

respect to the corresponding ones of the other monomer. Therefore, the frequency of this mode, displayed in Table 3 for the selected dimers, was attributed to the intermolecular stretching vibration of the dimer. For the ethane complex, the intermolecular stretching mode is split into symmetric and asymmetric components following the analysis of the computed normal vectors.

As revealed from the Table 3 results, both DFT−D and MP2 methods yield very comparable intermolecular stretching frequencies, especially for the longer alkanes. The discrepancy for the ethane dimer is a consequence of the different structures found with the two methods (Table 1). The MP2 dimer has a larger intermolecular distance, a smaller interaction energy, and thus a reduced intermolecular stretching frequency with respect to DFT−D. The molecular stretching C−C and C−H and bending CH$_2$ vibrations in all studied dimers are very close to those obtained for the isolated monomers, thus correlating with the results that the geometry changes of the *n*-alkane moieties in the dimers are negligible. Moreover, the molecular vibrational modes of both moieties are fully degenerate.

4. Conclusions

In this study, we have calculated the interaction energies of two isomers of trans *n*-alkane dimers, from ethane to dodecane, comparing the values and the trends provided by traditional correlated MP2 and CCSD(T) methods and by a DFT approach using the revised PBE exchange and LYP correlation functionals, augmented with an empirical dispersion correction. From the comparison, we have concluded that the DFT−D/cc-pVTZ results are in very good agreement with those obtained from MP2 for the geometries and from CCSD(T)(limit)/cc-pVTZ for the energies, the largest dimer compared being the hexane dimer.

The most stable isomers correspond to two alkane chains with their carbon skeletons in parallel planes, whereas in the other type of isomers, the two carbon skeletons are in the same plane. In both cases, the butane dimer is the first complex among the C$_n$ series for which regular trends for geometric and energetic properties are found to apply. Interestingly, the distance *d* between the two carbon skeletons from C$_4$ to higher alkanes remains constant, with a value of 4.09 Å for the most stable isomers and 3.96 Å for the second isomers. Both types of dimers have their alkane chains shifted one with respect to the other, allowing then the best CH$_2$·· ·CH$_2$ adjustment between the chains, in terms of the balance of electrostatic and exchange repulsion and long-range attraction. As a consequence, adding a CH$_2$ unit to a C$_n$

dimer, *n* > 4, generates a regular increase of stabilization for the dimer of about −0.8 kcal/mol due to dispersion. In relation with these trends, the symmetric stretching frequencies of the dimers are found constant at about 56−58 cm^{-1}, the five other far-infrared modes being coupled group rotations of the two dimer moieties.

The comparison between the results obtained from MP2/ G3(CCSD(T)) and revPBE-LYP, augmented with a dispersion correction, demonstrates the applicability of this DFT−D method to describing the properties of molecular clusters containing long alkane chains.

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