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Local MP2-Based Method for Estimation of Intermolecular Interactions in Aromatic Molecules. Benzene, Naphthalene, and Pyrimidine Dimers. A Comparison with Canonical MP2 Method

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Benzene, pyrimidine, and naphthalene dimers have been studied at canonical MP2, LMP2, and MP4(SDTQ) levels of theory. It has been shown that the LMP2 method is superior to canonical MP2 due to reduced BSSE. Thus, basis set limit-extrapolated LMP2 binding energies of T-shaped and parallel displaced (PD) benzene dimers are nearly the same, as has been found in higher level ab initio calculations. MP4(SDTQ) binding energies calculated at LMP2 optimized geometries are always more negative than those calculated for MP2-optimized geometries. MP4(SDTQ)/CC-pVDZ-corrected complete basis set-extrapolated LMP2 binding energies of T-shaped and PD dimers of benzene and naphthalene were found to be −2.80, −2.59 and −4.39, −6.29 kcal/mol, respectively.

Introduction

One of the major goals of chemistry in recent times has been the investigation and understanding of weak interactions.[1−6] Aromatic−aromatic interactions play important roles in many chemical and biological systems. They are important because of their effect on the base−base interactions leading to the double-helical structure of DNA, the function of the special pair in photosynthetic reaction centers, the packing of aromatic crystals, the formation of aggregates, the binding affinities in host−guest chemistry, and the conformational preferences of polyaromatic macrocycles.

Since dispersion interactions contribute most to binding energies between aromatic molecules, these energies can be calculated only by methods which take into account electron correlation. Density functional theory (DFT)-based methods allow one to include electron correlation at the lowest computational cost, but these methods are known to reproduce the dispersion interaction very poorly.[7] The most popular and not very time-consuming is the MP2 method, which has been widely used for studying of benzene,[8−10] naphthalene,[10−13] anthracene,[11] and pyrrole dimers.[14] However, the MP2 method also takes an inadequate amount of correlation. Thus, it has recently been shown that MP2 overestimates the binding energy by 30 and 92% for T-shaped and parallel benzene dimers, respectively, in comparison with CCSD(T) results.[8] Similar overestimation of binding energies was reported for naphthalene dimers.[10] Various approaches have been taken to remedy the deficiency of the MP2 method. The most straightforward one is the use of ab initio methods including high-order correlation corrections, such as MP4(SDTQ) and CCSD(T).[8,10] It has been shown that triple excitations are essential for correct description of intermolecular interactions.[10] MP4(SDQ) and CCSD values for binding energies in benzene dimers are from 12 to 27% lower compared to MP4(SDTQ) and CCSD(T) ones. Even for relatively small benzene dimers, correlation-consistent triple-ζ quality basis sets are not practical for present day computers to run MP4(SDTQ) or CCSD(T) calculations. Another approach consists of the introduction of high-order correlation corrections to the binding energy obtained at the MP2 level with large basis sets near saturation or MP2 binding energy extrapolated to the basis set limit.[9,15] CCSD(T) in combination with moderate basis sets is generally used to include high-order correlation corrections. These complex methods recover more correlation energy compared to pure MP4(SDTQ) or CCSD(T) methods, and one of the most complete up-to-date studies of benzene dimers based on the aromatic intermolecular interaction (AIMI) model predicts T-shaped and parallel displaced (PD) benzene dimers to be almost isoenergetic.

Local correlation methods have recently emerged as alternatives for the study of intermolecular interactions. Reduced step dependence of the computational cost on the size of molecule and reduced basis set superposition error (BSSE) are two important advantages of the local MP2 method (LMP2).[16] In particular, it has been shown that LMP2- and CP-corrected MP2 equilibrium geometries of water and water clusters are fairly close.[17] Although the LMP2 method has most of the intrinsic shortcomings of the canonical MP2 method, it shows superior performance, primarily due to nonexistent BSSE at the LMP2 level and lower scaling (N^3 instead of N^4 for conventional MP2), which allows one to use larger basis sets. Despite the evident advantages of LMP2 over MP2, this method has seldom been applied to intermolecular interactions.[18,19] Furthermore, there are no comparative studies between LMP2 and MP2 methods. The most important advantage of LMP2 compared to MP2 is the significant time savings. Hence, it may be very useful in treating interactions between large molecules. The goal of this paper is a detailed comparison between LMP2 and MP2 methods in terms of their suitability for studying intermolecular interactions between aromatic molecules.

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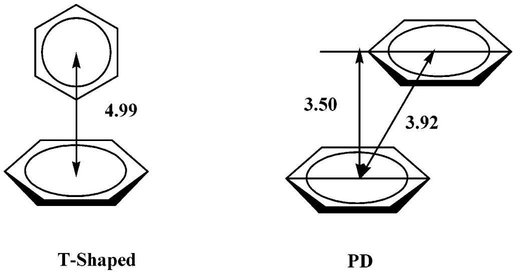


Figure 1. Geometry of benzene dimers.

TABLE 1: BSSE-Corrected Binding Energies of MP2/6-31G*-Optimized Benzene Dimers[a] at Different Levels of Theory

basis set	scf	MP2	LMP2	CCSD(T)[a]	MP4(SDTQ)
			PD		
6-31g	4.23	0.45	1.49	1.16	0.86
6-31g*	4.20	−0.50	0.63	0.63	0.27
6-311g*	3.80	−1.99	−0.30	−0.48	−1.06
6-311g**	3.79	−2.30	−0.55	−0.73	−1.34
cc-pvdz	3.81	−1.82(−2.00)[b]	−0.47	−0.39	−1.03
ccpvtz	3.71	−3.61	−2.09		
cc-pvqz	3.69	−4.20	−2.86		
basis set limit		−5.20	−3.56		
			T		
6-31g	1.01	−0.69	−0.07	−0.34	−0.48
6-31g*	0.94	−1.41	−0.69	−0.85	−1.02
6-311g*	0.90	−2.06	−1.01	−1.31	−1.58
6-311g**	0.93	−2.18	−1.16	−1.40	−1.68
cc-pvdz	0.93	−1.94(−2.02)[b]	−0.99	−1.23	−1.52
ccpvtz	0.98	−2.97	−2.21		
cc-pvqz	0.99	−3.31	−2.62		
basis set limit		−3.85	−3.30		

[a] Taken from ref 9. [b] Calculated with cc-pvdz (6D) basis with GAMESS program used for MP4 correction of LMP2 energies.

Computational Details

All geometry optimizations were carried out without any symmetry restrictions. LMP2 geometry optimizations and single-point energy evaluations were done with the Jaguar 4.2 suite of programs.[20] For the MP2 geometry optimizations and single-point energy evaluations, Gaussian 98, revision A9, was used.[21] LMP2-optimized structures were used as input for MP2 optimizations. Single-point MP4(SDTQ) energies were obtained with PC-GAMESS, version 6.2,[22] of the GAMESS (U.S.) package.[23] For all binding energies, a counterpoise correction term has been computed according to ref 24. For the benzene dimers, no geometry optimizations were done, and *Z*-matrices of MP2/6-31G*-optimized structures were taken from ref 9 for the purpose of comparison. Geometries of T-shaped and PD naphthalene dimers minimized at the LMP2/6-31G* level and used for single-point energy evaluations were taken from ref 18 and were used as starting structures for MP2/6-31G* optimizations of naphthalene dimers. MP2 and LMP2 energies at the basis set limit were estimated by extrapolation of interaction energy versus $1/N$, where N is the number of contracted atomic orbitals.[15]

Results and Discussion

Benzene Dimers. The most recent and the most complete study on benzene dimers used the MP2 complete basis set method with CCSD(T) correction for single-point energy evaluation. It predicts for T-shaped and PD dimers (Figure 1) stabilization energies of −2.46 and −2.48 kcal/mol, respectively.[9] Table 1 shows the binding energies of these complexes at different levels of theory. As can be seen, the MP2 method at the basis set limit predicts the PD dimer to be 1.35 kcal/mol more stable than the T-shaped dimer. On the other hand, the PD and T-shaped dimers show almost equal LMP2 binding energies at the basis set limit. The difference of binding energies at the basis set limit (0.26 kcal/mol) is in much better agreement with the results of high-level calculations than that for the canonical MP2 method, although the absolute values of the binding energies are still too negative. The improved performance of the LMP2 method may be due to the absence of BSSE. Since a BSSE correction does not eliminate the one completely, canonical MP2 overestimates the stability of the PD dimer due to strong overlapping of the basis functions at this geometry. This hypothesis can easily be confirmed from an inspection of SCF binding energies in Table 1. SCF binding energies are much more positive for the PD dimer relative to the T-shaped dimer due to stronger exchange repulsion.[18] A Kitaura−Morokuma energy decomposition analysis[25] carried out for benzene dimers with a 6-31G* basis set shows that exchange repulsion energies are 2.47 and 3.19 kcal/mol for the T-shaped and PD dimer, respectively. It has been argued[15] that local implementation of the MP2 method is inapplicable to delocalized systems such as benzene. The localization is, however, merely formal and does not change the values of physical observables.[26]

The CCSD(T) and LMP2 binding energies for benzene dimers are nearly equal, at least for a 6-311G** basis set. The reason for this agreement is not apparent, since the LMP2 method does not include high-order correlation corrections. The introduction of high-order correlation corrections would greatly improve the performance of the LMP2 method in the study of intermolecular interaction. Since triple excitations are important in a correct description of intermolecular interactions in benzene dimers, CCSD(T) or MP4(SDTQ) corrections to LM2 energies are needed. Less computationally demanding compared to CCSD(T), the MP4(SDTQ) method gives energies of comparable quality. This method was used to correct the LMP2 binding energies of benzene dimers. Table 2 shows the results of this correction, where the final binding energy is defined as LMP2 + ΔMP4(SDTQ), where

$$\Delta\mathrm{MP4(SDTQ)} = AB(\mathrm{MP2}-\mathrm{MP4}) - [(A(\mathrm{MP2}-\mathrm{MP4}) + B(\mathrm{MP2}-\mathrm{MP4})]$$

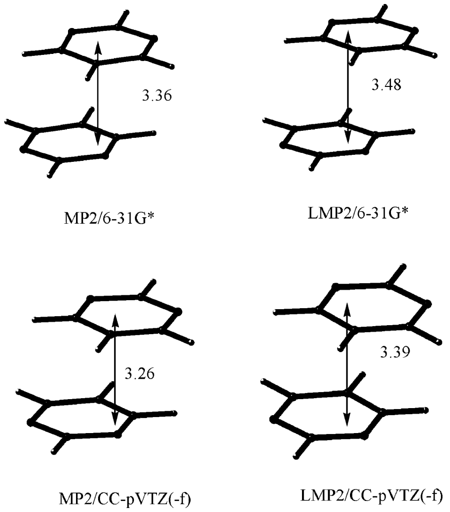
A and B are monomer units with ghost orbitals of the other monomer. As can be seen from Table 2, a 6-31G basis set is too small to significantly improve the binding energies. However, a 6-31G* basis set in combination with CBS LMP2 energies performs much better. As can be seen from Table 2, the inclusion of high-order correlation correction to the LMP2 energy decreases the binding energy and gives almost equal stabilization energies for the two dimers. Thus, the binding energies for MP4(SDTQ)/6-311G**- and MP4(SDTQ)/cc-pVDZ-corrected CBS LMP2 models in the case of T-shaped and PD dimers are −2.80 and −2.60 kcal/mol, in close agreement with the highest level calculations which have been done for those dimers.[9] Taking into account possible shortcomings of the extrapolation technique to obtain the LMP2 basis set limit energies, MP4(SDTQ) LMP2/cc-pVQZ-corrected binding energies also give results in agreement with the highest level calculations, which predict nearly isoenergetic T-shaped and PD structures. The most important point to mention is that, as follows from Table 2, the LMP2-based method converged to correct values with basis set size.

Pyrimidine Dimer. A comparison of the performance of MP2 and LMP2 optimizations was made for the pyrimidine dimer (Figure 2). Two basis sets were used in the optimization

TABLE 2: BSSE-Corrected Stabilization Energies (*E*, kcal/mol) of MP2/6-31G*-Optimized Benzene Dimers[a] Obtained Using MP4(SDTQ)-Corrected Complete Basis Set LMP2 Method[b]

LMP2	MP4(SDTQ)	E^b
	T	
ccpvtz	6-31g	−2.00
ccpvqz	6-31g	−2.41
basis set limit[c]	6-31g	−3.09
ccpvtz	6-31g*	−1.82
ccpvqz	6-31g*	−2.23
basis set limit	6-31g*	−2.91
ccpvtz	6-311g*	−1.73
ccpvqz	6-311g*	−2.14
basis set limit	6-311g*	−2.82
ccpvtz	6-311g**	−1.71
ccpvqz	6-311g**	−2.12
basis set limit	6-311g**	−2.80
ccpvtz	ccpvdz	−1.71
ccpvqz	ccpvdz	−2.12
basis set limit	ccpvdz	−2.80
	PD	
ccpvtz	6-31g	−1.68
ccpvqz	6-31g	−2.45
basis set limit	6-31g	−3.15
ccpvtz	6-31g*	−1.32
ccpvqz	6-31g*	−2.09
basis set limit	6-31g*	−2.79
ccpvtz	6-311g*	−1.16
ccpvqz	6-311g*	−1.93
basis set limit	6-311g*	−2.63
ccpvtz	6-311g**	−1.13
ccpvqz	6-311g**	−1.90
basis set limit	6-311g**	−2.60
ccpvtz	ccpvdz	−1.12
ccpvqz	ccpvdz	−1.89
basis set limit	ccpvdz	−2.59

[a] Molecular geometry taken from ref 9. [b] Total stabilization energy is defined as LMP2 + ΔMP4(SDTQ), where ΔMP4(SDTQ)= *AB*(MP2−MP4) − [(*A*(MP2−MP4) + *B*(MP2−MP4)], where *A* and *B* are corresponding monomer units with ghost orbitals of the second monomer. [c] LMP2 energies at the basis set limit were estimated by extrapolation of interaction energy versus 1/*N*, where *N* is the number of contracted atomic orbitals.



MP2/6-31G* LMP2/6-31G*

MP2/CC-pVTZ(-f) LMP2/CC-pVTZ(-f)

Figure 2. Geometry of pyrimidine dimer optimized at different levels of theory.

procedures: a standard 6-31G* and a correlation-consistent triple-ζ basis set with f-functions removed (CC-pVTZ(-f)). An extensive computational study of the pyrimidine dimer predicts the binding energy for this dimer to be −3.4 kcal/mol. This result was obtained from a CCSD(T)-corrected CBS MP2 single-point energy evaluation using rigid monomer optimized geometry.[15] As can be seen from Figure 2, there is qualitative agreement between LMP2- and MP2-optimized geometries of pyridine dimers. However, LMP2 predicts larger interplane distances between monomers than does the canonical MP2 method. Optimization with a CC-pVTZ(-f) basis set gives a tighter complex at either MP2 or LMP2 levels of theory than does the smaller 6-31G* basis set (Figure 2).

TABLE 3: Binding Energies (kcal/mol) of Pyrimidine Dimer Calculated at Different Levels of Theory

basis Set[a]	SCF	MP2	MP4 (SDTQ)	LMP2	$E_1{}^a$	$E_2{}^b$
LMP2/cc-pVTZ(-f)						
6-31G*	2.82	−2.28	−1.54	−0.78		
cc-pVDZ	2.88	−2.80	−2.09	−1.12		
cc-pVTZ	2.71	−4.64		−2.71		
cc-pVQZ	2.48	−5.27		−3.95	−3.07	−4.42
basis set limit		−6.25		−4.75	−3.90	−5.4
MP2/cc-pVTZ(-f)						
6-31G*	4.75	−1.68	−0.81	0.08		
cc-pVDZ	4.82	−2.40	−1.49	−0.30		
cc-pVTZ	4.66	−4.61	-	−2.36		
cc-pVQZ	4.61	−5.39	-	−3.63	−2.55	−4.31
basis set limit		−6.60		−4.75	−3.67	−5.52
LMP2/6-31G*						
6-31G*	1.69	−2.29	−1.72	−1.07		
cc-pVDZ	1.76	−2.72	−2.18	−1.35		
cc-pVTZ	1.61	−4.25		−2.70		
cc-pVQZ	1.59	−4.77		−3.73	−3.06	−4.10
basis set limit		−5.50		−4.50	−3.83	−4.83
MP2/6-31G*						
6-31G*	4.53	−1.83	−0.91	−0.05		
cc-pVDZ	4.60	−2.47	−1.59	−0.43		
cc-pVTZ	4.46	−4.65		−2.46		
cc-pVQZ	4.41	−5.42		−3.73	−2.69	−4.38
basis set limit		−6.52		−4.75	−3.71	−5.48

[a] Total stabilization energy is defined as LMP2 + ΔMP4(SDTQ), where ΔMP4(SDTQ) = *AB*(MP2−MP4) − [(*A*(MP2−MP4) + *B*(MP2−MP4)], where *A* and *B* are corresponding monomer units with ghost orbitals of the second monomer and MP4(SDTQ) energy is calculated with cc-pVDZ basis set. LMP2 energies at the basis set limit were estimated by extrapolation of interaction energy versus 1/*N*, where *N* is the number of contracted atomic orbitals. [b] Total stabilization energy is defined as MP2 + ΔMP4(SDTQ), where ΔMP4(SDTQ) = *AB*(MP2−MP4) − [(A(MP2−MP4) + *B*(MP2−MP4)], where *A* and *B* are corresponding monomer units with ghost orbitals of the second monomer and MP4(SDTQ) energy is calculated with the cc-pVDZ basis set.

Stabilization energies of the pyridine dimer at the MP2 level, which were reported in ref 15, are higher by 0.5−1 kcal/mol for given basis sets (6-31G*, CC-pVTZ, and CC-pVQZ). The claim[15] that rigid monomer and gradient-optimized geometries are equally suitable is not valid in this case. Fully optimized structures are significantly lower in energy. When comparing MP2 and LMP2 binding energies at different geometries, one can see that LMP2/CC-pVQZ and LMP2 energies at the basis set limit are much less sensitive to the optimization method compared to the canonical MP2 model, being in the range from −3.63 to −3.95 and from −4.50 to-4.75 kcal/mol, respectively, while binding energies calculated with MP2 range from −5.50 to −6.52 and from −4.77 to −5.42 kcal/mol for basis set limit and CC-pVQZ basis set, respectively. Apparently, this difference can be rationalized in terms of the reduced BSSE of the LMP2 method since BSSE correction does not eliminate BSSE completely.

It is interesting to note that there is a significant difference between binding energies calculated at the MP4(SDTQ) level of theory at different geometries. As can be seen from Table 3, in all cases MP4(SDTQ) stabilization energies are more negative for LMP2-optimized geometries. These numbers indicate that the LMP2-optimized structure is closer to a minimum on the MP4(SDTQ) potential energy surface for the pyrimidine complex than is the MP2-optimized structure.

As in the case of benzene dimers, high-order correlation contributions from MP4(SDTQ)/CC-pVDZ single-point energy calculations were used to correct LMP2 and MP2 stabilization energies. As can be seen from Table 3, LMP2-corrected stabilization energies at the basis set limit are 1−2 kcal/mol less negative than the MP2-corrected values. The range from −3.67 to −3.90 kcal/mol, depending on the geometry optimization method used. Complete basis set MP2 binding energies estimated for pyrimidine dimer in ref 15 are in the range −5.3 to 5.4 kcal/mol, less negative than the results obtained by the present authors, −5.50 to −6.52 kcal/mol, depending on the geometry optimization method (Table 3). As has been mentioned above, this difference is a consequence of the geometry optimization method employed. Apparently, the full optimization method used in this work allows one to locate structures closer to the minimum than does the rigid monomer optimization technique used in ref 15. It seems that the most reliable stabilization energies for pyrimidine dimer can be considered to be those calculated at the LMP2/CC-pVTZ(-f)-optimized structure, being of −3.90 kcal/mol (Table 3), which differs by 0.5 kcal/mol with that reported in ref 15.

Naphthalene Dimers. The LMP2 method is much less computationally demanding than is the canonical MP2 method, and it produces reliable results superior to those obtained with the canonical MP2 method. Hence, it is interesting to study larger aromatic dimers using LMP2 in conjunction with the complete basis set extrapolation technique with generally available computational recourses; a calculation is unfeasible using canonical MP2 for a species as large as the naphthalene dimer. The present authors have already published an LMP2 study of aromatic dimers, including naphthalene.[18] Other authors published a study of naphthalene dimers at the MP2/6-31G* level of theory.[13] The lowest energy conformer was found to be the parallel-displaced dimer with approximate C_i symmetry at the LMP2/aug-CC-pVTZ(-f)//LMP2/6-31G* level of theory. This conformer has a stabilization energy of −7.72 kcal/mol. Of the T-shaped geometries, the most stable conformer was found to be the one shown in Figure 3. It has a stabilization energy of −3.96 kcal/mol at the same level of theory. In a recent work on naphthalene dimers, the same dimers were found to be the most stable ones at the MP2/6-31G* (0.25) level using a point-by-point optimization method with BSSE correction. The stabilization energies found were estimated to be −6.36 and −4.25 kcal/mol at the MP2/6-31+G* level.[12]

Figure 3 shows LMP2/6-31G*- and MP2/6-31G*-optimized geometries of T and PD naphthalene dimers. As can be seen from the Figure 3, LMP2- and MP2-optimized geometries are qualitatively similar to one another. The LMP2-optimized dimers have larger monomer−monomer separation, similar to that calculated for the pyrimidine complex (Figure 2).

It is interesting to compare the quality of LMP2- and MP2-optimized geometries with respect to MP4(SDTQ) binding energies (Table 4). As in the pyrimidine case, MP4(SDTQ) binding energies for both types of complexes, T-shaped and PD, are more negative for LMP2-optimized geometries, showing that LMP2-optimized geometries are closer to a minimum on the MP4(SDTQ) potential energy surface than are MP2-optimized geometries. Most likely, this difference is related to the reduced BSSE of the LMP2 method.

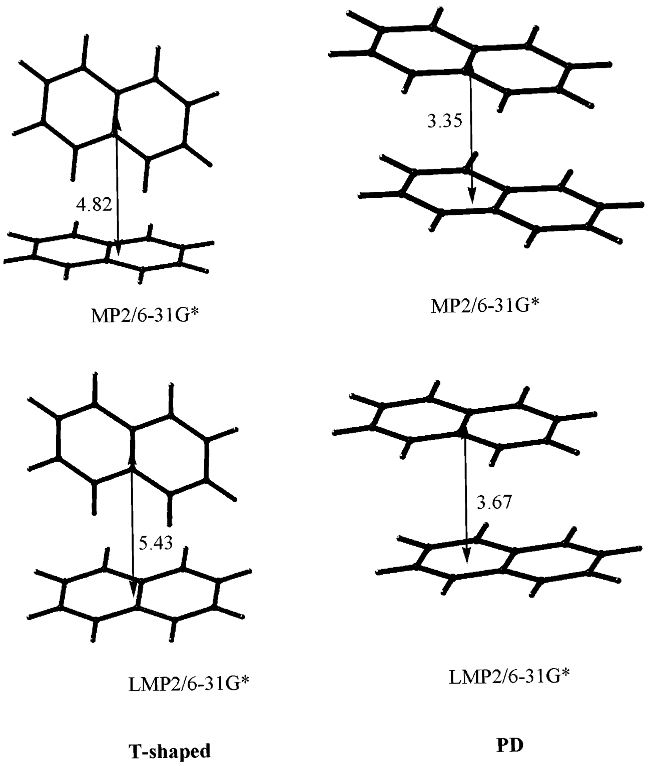


Figure 3. MP2/6-31G*- and LMP2/6-31G*-optimized geometries of T-shaped and PD naphthalene dimers.

TABLE 4: Binding Energies of PD and T-Shaped Naphthalene Dimers (kcal/mol) Optimized at LMP2/6-31g* and MP2/6-31G* Levels

basis set	LMP2	MP4(SDTQ)	E^a
	PD		
LMP2/6-31g*			
cc-pVDZ	−2.10	−3.83	−0.39
cc-pVTZ	−4.88		−3.17
cc-pVQZ	−6.26		−4.55
basis set limit	−8.00		−6.29
MP2/6-31G*			
cc-pVDZ	−0.28	−3.29	2.53
cc-pVTZ	−4.39		−1.58
cc-pVQZ	−6.59		−3.78
basis set limit	−8.70		−5.89
	T-Shaped		
LMP2/6-31g*			
cc-pVDZ	−2.16	−3.22	−1.55
cc-pVTZ	−3.73		−3.12
cc-pVQZ	−4.17		−3.56
basis set limit	−5.00		−4.39
MP2/6-31G*			
cc-pVDZ	−0.97	−2.84	0.21
cc-pVTZ	−3.60		−2.42
cc-pVQZ	−5.26		−4.08
basis set limit	−6.50		−5.32

[a] Total stabilization energy is defined as LMP2 + ΔMP4(SDTQ), where ΔMP4(SDTQ) = *AB*(MP2−MP4) − [(*A*(MP2−MP4) + *B*(MP2−MP4)], where *A* and *B* are corresponding monomer units with ghost orbitals of the second monomer and MP4(SDTQ) energy is calculated with the cc-pVDZ basis set.

LMP2 stabilization energies depend on the geometry optimization method. Thus, extrapolated LMP2 complete basis set energies are from 0.7 to 1.5 kcal/mol more negative for MP2-optimized geometries, but there are no qualitative differences between the two optimization methods. In the case of naphthalene dimers, the LMP2 and MP2 methods are similar in predicting the PD dimer to be more stable than the T-shaped dimer. The LMP2 energy difference in stability between the two dimers is 3 kcal/mol at the basis set limit and 2.09 kcal/mol at the LMP2/CC-pVQZ//LMP2/6-31G* level. The canonical MP2 method predicts the PD dimer to be more stable by 2.11 kcal/mol at the MP2/6-31+G*//MP2/6-31G* level of theory,[12] in qualitative agreement with MP4(SDTQ)/CC-pVDZ binding energies (Table 4) and with the prediction that PD structures become more stable compared to T-shaped structure as the size of the aromatic molecule increases. This fact reveals the importance of correlation stabilization for aromatic dimers, which is stronger for PD dimers. Correlation stabilization increases with the size of the molecule for PD dimers much stronger than it does for T-shaped dimers.

As in the case of benzene dimers, the MP4(SDTQ) correction to the LMP2 binding energy decreases the energy gap between PD and T-shaped dimers, giving final energies of −6.29 and −4.29 kcal/mol, respectively, for the PD and T-shaped dimers (Table 4).

Conclusions

Many of the shortcomings of the MP2 method are related not to the method itself but to BSSE, which is not eliminated completely by the BSSE correction scheme. Thus, LMP2 predicts similar stabilization energies for PD and T-shaped benzene dimers in the basis set limit, which agree with methods which take into account high-order correlation contributions. LMP2-optimized geometries give more negative stabilization energies at the MP4(SDTQ) level than do MP2-optimized geometries for all the dimers studied. Thus, the LMP2 method for geometry optimization of aromatic dimers appeared to be preferable to the canonical MP2 method. When high-order correlation corrections from MP4(SDTQ) calculations are made to the LMP2 stabilization energies, the resulting stabilization energies agree within 0.2−0.3 kcal/mol with those calculated at the highest theoretical level, and the computational cost is significantly lower. This method was used to estimate stabilization energies of naphthalene dimers and can be applied to larger aromatic systems to obtain precise stacking energies at relatively low computational cost.

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