FEATURE ARTICLE

Understanding of Assembly Phenomena by Aromatic−Aromatic Interactions: Benzene Dimer and the Substituted Systems

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Interactions involving aromatic rings are important in molecular/biomolecular assembly and engineering. As a consequence, there have been a number of investigations on dimers involving benzene or other substituted π systems. In this Feature Article, we examine the relevance of the magnitudes of their attractive and repulsive interaction energy components in governing the geometries of several $\pi-\pi$ systems. The geometries and the associated binding energies were evaluated at the complete basis set (CBS) limit of coupled cluster theory with singles, doubles, and perturbative triples excitations [CCSD(T)] using a least biased scheme for the given data set. The results for the benzene dimer indicate that the floppy T-shaped structure (center-to-center distance: 4.96 Å, with an axial benzene off-centered above the facial benzene) is isoenergetic in zero-point-energy (ZPE) corrected binding energy (D_0) to the displaced-stacked structure (vertical interplanar distance: 3.54 Å). However, the T-shaped structure is likely to be slightly more stable ($D_0 \approx 2.4-2.5$ kcal/mol) if quadruple excitations are included in the coupled cluster calculations. The presence of substituents on the aromatic ring, irrespective of their electron withdrawing or donating nature, leads to an increase in the binding energy, and the displaced-stacked conformations are more stabilized than the T-shaped conformers. This explains the wide prevalence of displaced stacked structures in organic crystals. Despite that the dispersion energy is dominating, the substituent as well as the conformational effects are correlated to the electrostatic interaction. This electrostatic origin implies that the substituent effect would be reduced in polar solution, but important in apolar media, in particular, for assembling processes.

I. Introduction

Interactions involving aromatic rings[1] are widely prevalent in clusters, biomolecules, organic/biomolecular crystals, and nanomaterials. Crystals with aromatic molecules are often self-assembled by π interactions,[2−4] and the aromatic rings of Trp, His, Tyr, and Phe in proteins bind either other aromatic rings (π-π or π-H interaction) or hydrogen donors (π-H interactions).[5] The energetic and geometrical significance of π interactions in stabilizing the $\pi-$involving systems has been extensively investigated.[6−27] Furthermore, recent advances, which include self-assembly of organic nanotube bundles,[3] mechanical extraction of inner-shells from multi-walled carbon nanotubes,[28] and controlled flapping motion of molecular flippers as a precursor of nanomechanical devices or nanovehicles,[29] have highlighted the utility of harnessing the aromatic−aromatic interactions in designing functional nanomaterials (Figure 1). Because most of the experimentally observed aromatic−aromatic interactions involve substituted aromatic

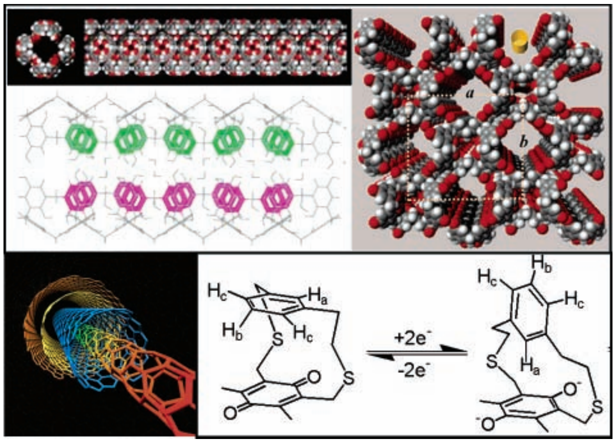

Figure 1. Aromatic-interaction-driven assembly of organic nanotube bundles (reproduced from ref 3a/c with permission from the American Chemical Society; copyright 2001/2002), extraction of inner-shells from mutliwalled carbon nanotubes (ref 28), and flapping motion of molecular flippers as nanomechanical devices (reproduced from ref 29 with permission from the American Chemical Society; copyright 2002).

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systems, it is useful to examine the role of the substituent in stabilizing the observed conformational motif.

The relative stability between the displaced-stacked (face-to-face) and the T-shaped (edge-to-face) aromatic−aromatic interactions has been the focus of several studies. In the gas-phase studies of the benzene dimer that were pioneered by Klemperer and co-workers[6] followed by Schlag and others,[7,8] the T-shaped conformers seem to be more favored.[7,8] However, in some studies the displaced-stacked conformers were also present.[8b] On the other hand, in crystals, aromatic rings exhibit displaced-stacked conformers more frequently than T-shaped conformers.[2−4] To explain these experimental observations, one needs to understand the energetic basis of T-shaped vs displaced-stacked conformational stability. In this regard, a number of theoretical calculations have been carried out.[9−15] Recently, there have been great efforts to make the density functional theory (DFT) obtain $\pi-\pi$ interaction energies.[16−20] Theoretical studies of the substituent effects on the aromatic systems were also investigated.[11−14,20−22] It is important to note that subtle variations in various components of the interaction energy can dramatically alter the conformational preferences.[11,12,14] Therefore, an accurate knowledge of the various interaction energy components would be useful in the fields of both nanomaterial design[30,31] and drug discovery.[32]

Based on experimental investigations of the relevant model compounds and crystal structures,[23−27] early interpretations of the nature of $\pi-\pi$ interactions by Hunter, Sanders, Cozzi, and Siegel.[23,24] were largely attributed to be electrostatic in nature. However, Wilcox and co-workers highlighted the important role of dispersion energies.[26] All these interpretations have been extensively corroborated by a number of experimental and theoretical investigations of $\pi-\pi$ interactions. A significant outcome of this electrostatic vs dispersion debate on $\pi-\pi$ interactions is that the substituent effects would not be significant in polar solution, if the interactions are electrostatic in nature. Because this is an extremely important issue in understanding protein structures and assembly phenomena involving $\pi-\pi$ interactions, high-level quantum chemical investigations are essential.

One of the most challenging issues in quantum chemical calculations of aromatic systems is the need to obtain accurate estimates of the dispersion energy. The description of the dispersion energy is affected by both the level of theory employed and the size of the basis set used. Most investigations employing DFT predict the stacked conformer to be unstable. This is because of the fact that most density functionals do not properly take into account dispersion energies. On the other hand, second-order Møller−Plesset perturbation theory (MP2) calculations using small basis sets predict that both displaced-stacked and T-shaped conformers are nearly isoenergetic. The use of large basis sets at the MP2 level leads to the stabilization of the displaced-stacked conformer by about ~1 kcal/mol. On the other hand, the use of moderately sized basis sets at the CCSD(T) leads to the stabilization of the T-shaped conformer. It has, however, been conjectured that the displaced-stacked conformer could be energetically stabilized using very large basis sets, i.e., at the CBS limit of the CCSD(T) level. Despite the presence of several studies that include rough estimates of the CCSD(T)/CBS energies, one needs a more accurate value of the interaction energy of the benzene dimer. This would provide a more efficient scaffold for discussing substituent effects.

Substituent effects have theoretically been investigated by Sherrill and co-workers[14] and us.[11,33] Though Sherrill et al. highlighted the importance of dispersion energies,[14] the total $\pi-\pi$ interaction energy could not be correlated to the substituent effects. In a recent study, we had shown that the extra stablization energy mainly accrues from electrostatic energies. This is because the dominant dispersion energy to a large extent is cancelled out by the repulsive exchange energies in the equilibrium geometries.[11]

In this work, we focus on the accurate evaluation of both the geometry and binding energy of $\pi-\pi$ interactions. In addition to the benzene dimer, we have also considered both the stacked and T-shaped conformers in their fully relaxed geometries. We compare several substituted benzene−benzene complexes (PhX: Bz) where X = H, CH_3, OH, NH_2, F, CN, and NO_2. Additionally, we also elucidate the origin of these aromatic−aromatic interactions in terms of energy components (electrostatic, induction, dispersion, and exchange energies) and examine their importance in understanding self-assembling phenomena and designing nanomaterials.

II. Methods

In this work, the potential energy surface of the benzene dimer has been examined with respect to all possible degrees of freedom. A number of structures possessing various symmetries were optimized at both the conventional and the resolution of the identity approximation (RI)[34] of the second-order Møller−Plesset perturbation theory (MP2) using the aug-cc-pVDZ (abbreviated as aVDZ) basis set. The differences in MP2 and RI-MP2 optimized structures and energies are insignificant (≤0.01 Å and ≤0.05 kcal/mol in most cases). Furthermore, the relative differences in binding energies between different conformers are negligible (<0.02 kcal/mol in most cases) because of the cancellation of errors, as the errors are consistent. Armed with this information, we examined the substituent effects in both stacked and T-shaped complexes, by carrying out optimizations at the MP2/6-31+G* and RI-MP2(Full)/aVDZ levels with all the electrons correlated. The basis-set-superposition-error (BSSE) corrected interaction energies (ΔE_e) and these zero-point-energy (ZPE) corrected interaction energies (ΔE_0) were taken into account. The energy decomposition of the BSSE-corrected RI-MP2/aVDZ geometries into the individual electrostatic, induction, dispersion, and exchange repulsion components was carried out using the symmetry adapted perturbation theory (SAPT)[35] coupled to an Atmol interface.[36] In this case, we used the aVDZ′ basis set wherein the p diffuse functions of the H atoms and the d diffuse functions for the heavy atoms are deleted from the conventional aVDZ basis set. For the sake of comparison, SAPT/aVDZ calculations were also carried out for the benzene dimer.

The binding energies ($D_e = -\Delta E_e$) for various conformers of the benzene dimer were obtained with the inter-phenyl distance optimized in consideration of BSSE corrections. The energies of these BSSE-corrected optimized structures were evaluated at the RI-MP2 level using the aVDZ, aug-cc-pVTZ (abbreviated as aVTZ), and aug-cc-pVQZ (abbreviated as aVQZ) basis sets. CCSD(T) calculations using aVDZ and aVTZ basis sets were also performed on the BSSE-corrected optimized structures.

The ab initio calculations were carried out using the Turbomole[37] 5.6 and Molpro[38] 2002.6 packages. POSMOL[39] was used for drawing the molecular structures. For large basis sets [RI-MP2/aV*N*Z (N = D, T, Q, ..., i.e., $N = 2, 3, 4, ...$)] full-BSSE correction was carried out. However, for calculations involving small basis sets such as MP2/6-31+G* and CCSD-(T)/aVDZ′, 50%-BSSE correction was used (ΔE^h).[1b,40] The SAPT calculations were done with full-BSSE correction. For the evaluation of the CBS limit values, the frozen core (FC) approximation was employed for all the RI-MP2 and CCSD(T) calculations.

The CBS limit values at the RI-MP2 and CCSD(T) levels were obtained by taking into account both the BSSE-corrected (E^b_N) and BSSE-uncorrected (E^n_N) values.[41] Earlier evaluations of the energies at the CBS limit ignore BSSE-uncorrected energies.[42] The justification for using the BSSE-uncorrected energy is the fact that both the BSSE-uncorrected and -corrected energies eventually converge to the same asympototic value ($E_{CBS} = E^b_\infty = E^n_\infty$).[43] Thus, the asymptotic value based on extrapolation using both E^b_N and E^n_N could be considered as pseudo-interpolation in terms of energies because

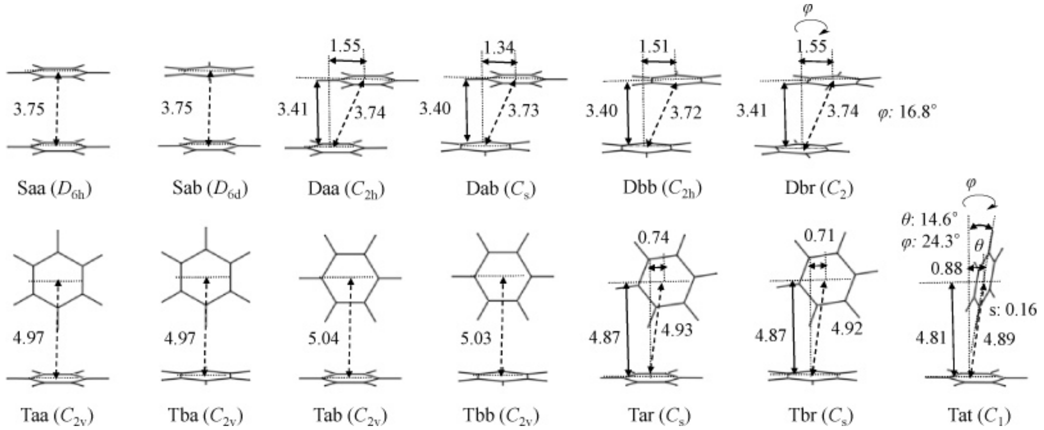

Figure 2. Selected conformations of the benzene dimer at the RI-MP2(Full)/aVDZ level (with the BSSE-corrected inter-phenyl distance in Å). See Table 1 for more accurate structures and binding energies. At the CCSD(T)/CBS level, the lowest energy structure is Tbr ∼ Tar ∼ Tat (Tbr: $r_{cc} = 4.96$ Å, $r_h = 0.77$ Å) with the binding energy 2.84 kcal/mol, and the lowest energy structure among the face-to-face conformers is Daa ∼ Dab ∼ Dbr (Daa: $r_v = 3.54$ Å, $r_{cc} = 3.95$ Å, $r_h = 1.74$ Å) with the binding energy 2.73 kcal/mol (Table 1)

E_{CBS} is between $E^b{}_N$ and $E^n{}_N$. Asymptotic values based on only $E^b{}_N$ ($>E^b{}_\infty$) would be inferior because $E^b{}_{N=\infty}$ needs to be obtained by extrapolation based on only a set of few energy values of $E^b{}_{N=2}$, $E^b{}_{N=3}$, $E^b{}_{N=4,}$ ... (despite that $N = 2/3/4$ is extremely far from $N = \infty$) with no single information of the lower bound.

Using an arbitrarily trained exponent only for $\Delta E^b{}_N$, we obtain an unbiased CBS limit value by expanding both $\Delta E^b{}_N$ and $\Delta E^n{}_N$ for aV*N*Z basis sets in the power series of $1/N$ (where the first leading term has a positive effective exponent x) and by forcing both asymptotic values to merge to the same value (ΔE_∞) at $N = \infty$ or $1/N = 0$. Therefore, we have

$$\Delta E^b{}_N = \Delta E_\infty + BY_N + CY_N{}^2 + ... \tag{1a}$$

and

$$\Delta E^n{}_N = \Delta E_\infty + B'Y_N + C'Y_N{}^2 + ... \tag{1b}$$

where

$$Y_N = N^{-x} \tag{2}$$

Here, ΔE_∞, x, B, B', C, C', ... need to be optimized.

The solution of eq 1 for the given sequential energies of E_N, E_{N+1}, E_{N+2}, ..., can be obtained from

$$\delta_N = (B - B')Y_N + (C - C')Y_N{}^2 + ... \tag{3}$$

and

$$\epsilon_N = 2\epsilon_\infty + (B + B')Y_N + (C + C')Y_N{}^2 + ... \tag{4}$$

where

$$\delta_N = \Delta E^b{}_N - \Delta E^n{}_N \tag{5}$$

and

$$\epsilon_N = \Delta E^b{}_N + \Delta E^n{}_N \tag{6}$$

As an example, if there are three consecutive energies, eq 3 has three equations for δ_N, δ_{N+1}, and $\delta_{N+2.}$ Then, three unknown parameters ($B - B'$, $C - C'$, x) can be solved by fitting. From three eqs 4 for ϵ_N, ϵ_{N+1} , and ϵ_{N+2}, the three remaining unknown parameters ($B + B'$, $C + C'$, ϵ_∞) can be obtained. In the particular case of two sequential energies E_N and E_{N+1}, one can easily find

$$\Delta E_\infty = {}^1/_2(\delta_N\, \epsilon_{N+1} - \delta_{N+1}\, \epsilon_N)/(\delta_N - \delta_{N+1}) \tag{7}$$

Thus, the CBS value is readily obtained even with only two energies corresponding to the aVDZ and aVTZ basis sets, without any parameters.

As for eq 1, we exploited the mathematical theorem that any two points can be best represented by a linear line ($C = C' = 0$), any three points can be best represented by a parabolic equation, and so on. It should be noted that the CBS value is obtained without any predetermined parameter (based on a training data set). All these estimations have been utilized for the benzene dimer in this Feature Article [three data points ($N = 2-4$) for MP2, and two data points ($N = 2-3$) for CCSD(T)]. The CBS limit for geometry can be done in a similar way.

The large size and lack of symmetry precluded the carrying out of CCSD(T)/aVTZ calculations on complexes of substituted aromatic rings. Therefore, in consideration that the binding energy difference between CCSD(T) and RI-MP2 at the aVDZ level does not change significantly with the increasing size of the basis set,[14,44] we estimate the CCSD(T)/CBS energies from CCSD(T)/aVDZ energies [$E_{CCSD(T)/CBS} = E_{RI-MP2/CBS} + (E_{CCSD(T)/aVDZ} - E_{RI-MP2/aVDZ})$].

III. Results

A. Benzene Dimer. Selected RI-MP2/aVDZ optimized structures and binding energies are shown in Figure 2. Prefixes “S”, “D”, and “T” denote “stacked”, “displaced-stacked”, and “T-shaped”, respectively, and suffixes a, b, r, and t denote CH *a*toms on the horizontal/vertical axis, the C═C *b*ond on the axis, the *r*otated axis, and *t*wisted. For the representative low-energy structures (Sab, Daa, Dbr, Tba, Tbr, Tat), the inter-phenyl distances and energies calculated at various levels of theory and their CBS limit RI-MP2 and CCSD(T) values are shown in Table 1. ΔE_{CBS} was obtained in two ways: (i) single-point energies for larger basis sets on the RI-MP2/aVDZ geometries with the inter-phenyl distance optimized with the BSSE correction, and (ii) energies for larger basis sets on the RI-MP2/aVDZ geometries with the inter-phenyl distance optimized by the BSSE correction at the given level of theory. It can be seen from the plots in Figure 3 that both ΔE^b and ΔE^n converge and yield ΔE_{CBS} values of −2.73 and −2.84 kcal/mol for conformers Daa and Tbr. The potential surface for T-shaped conformers

TABLE 1: Inter-Phenyl Distances (Å) and Binding Energies (D_e/kcal/mol) of Selected Conformers for the Benzene Dimer[a]

		displaced-stacked		T-shaped		
	stacked Sab ≈ Saa	Daa ≈ Dab (≈Dbb)	Dbr	Tba ≈ Taa	Tbr ≈ Tar	Tat
			RI-MP2/FC: $\{r_\mathrm{h}\}/r_\mathrm{v}$ $[r_\mathrm{cc}]$			
	{0.00}/	{1.55}/	{1.55}/	{0.00}/	{0.71}/	{0.88}/
aVDZ	3.75 [3.75]	3.41 [3.74]	3.41 [3.74]	4.97 [4.97]	4.87 [4.93]	4.81 [4.89]
aVTZ	3.69 [3.69]	3.34 [3.69]	3.35 [3.69]	4.88 [4.88]	4.79 [4.85]	4.73 [4.81]
aVQZ	3.68 [3.68]	3.33 [3.67]	3.33 [3.67]	4.86 [4.86]	4.78 [4.83]	4.71 [4.80]
est-CBS	3.67 [3.67]	3.32 [3.66]	3.32 [3.66]	4.85 [4.85]	4.77 [4.82]	4.70 [4.79]
			RI-MP2/FC: D_e			
aVDZ	2.91	4.29	4.28	3.17	3.32	3.34
aVTZ	3.22 (3.23)	4.71 (4.76)	4.71 (4.75)	3.46 (3.51)	3.59 (3.63)	3.63 (3.67)
aVQZ	3.32 (3.35)	4.85 (4.93)	4.85 (4.93)	3.54 (3.61)	3.67 (3.74)	3.71 (3.78)
est-CBS	3.38 (3.42)	4.93 (5.03)	4.93 (5.03)	3.58 (3.66)	3.72 (3.80)	3.75 (3.84)
			CCSD(T)/FC: $\{r_\mathrm{h}\}$ r_v $[r_\mathrm{cc}]$			
aVDZ	3.97	{1.80} 3.62 [4.04]	{1.77} 3.61 [4.02]		{0.76} 4.98 [5.03]	{0.90} 4.92 [5.01]
aVTZ	3.92	{1.75} 3.56 [3.97]			{0.77} 4.91 [4.97]	
est-CBS	**3.91**	**{1.74} 3.54 [3.95]**			**{0.77} 4.90 [4.96]**	
			CCSD(T)/FC: D_e			
aVDZ′	0.18/1.34*	0.85/2.43*	0.82/2.39*	1.58/2.74*	1.66/2.81*	1.62/2.78*
aVDZ	1.10 (1.34)	2.06 (2.32)	2.04 (2.31)	2.34	2.46 (2.50)	2.45 (2.50)
aVTZ	1.35 (1.51)	2.4 1(2.57)		2.61	2.70 (2.71)	
est-CBS	1.53 **(1.66)**	2.62 **(2.73)**		2.77	2.84 **(2.84)**	

[a] See Figure 1 for the cluster structures. Taa and Tab are not given here because their binding energies are ~0.5 kcal/mol higher than those for Tbr/Tar/Tat at the RI-MP2(Full)/aVDZ level. The D_e values without parentheses were obtained on the RI-MP2(Full)/aVDZ geometries for which the interphenyl distance was optimized with BSSE-correction at the RI-MP2(Full)/aVDZ level. The D_e values in parentheses were obtained for the optimized inter-phenyl distance ($\{r_\mathrm{h}\}$, off-center distance; r_v, vertical distance; $[r_\mathrm{cc}]$, center-to-center distance) at the given level of theory, and other geometrical parameters are those of RI-MP2(Full)/aVDZ geometries. All the values reported here were calculated with the frozen core (FC) approximation. The RI-MP2(FC)/aVDZ//RI-MP2(Full)/aVDZ energies are slightly different from the RI-MP2(Full)/aVDZ energies in Figure 2. The values marked with an asterisk (*) for CCSD(T)/aVDZ′ denote the case with 50%-BSSE correction. It is interesting to note that the 50%-BSSE-corrected MP2/6-31+G* energies (not shown here) are close to the full-BSSE-corrected RI-MP2/aVDZ energies, and the 50%-BSSE-corrected CCSD(T)/aVDZ′ energies are close to the full-BSSE-corrected CCSD(T)/aVTZ and CCSD(T)/CBS energies. This information would be useful to estimate the interaction energies of large systems. For midsize basis sets with small diffuse functions such as MP2/6-31+G* and CCSD-(T)/aVDZ′, 50%-BSSE correction tends to be more realistic due to the insufficient recovery of dispersion energy, whereas for basis sets with large diffuse basis functions (larger than aVDZ), the BSSE-corrected binding energies are more realistic due to the overestimated BSSE by the diffuse nature of the basis set. The r_cc for Tbr at the CCSD(T)/CBS level (which is 0.14 Å smaller than the RI-MP2/CBS value) is in excellent agreement with the experimental value (4.96 Å: ref 8b). The r_v for Daa at the CCSD(T)/CBS level (3.54 Å) (which is 0.22 Å smaller than the RI-MP2/CBS value) is in reasonable agreement with the crystal data (3.3−3.6 Å: refs 2 and 49) for the displaced-stacked aromatic compounds. The most reliable CCSD(T)/CBS optimized interphenyl distances and the corresponding CCSD(T)/CBS optimized geometries and energies are highlighted in bold characters.

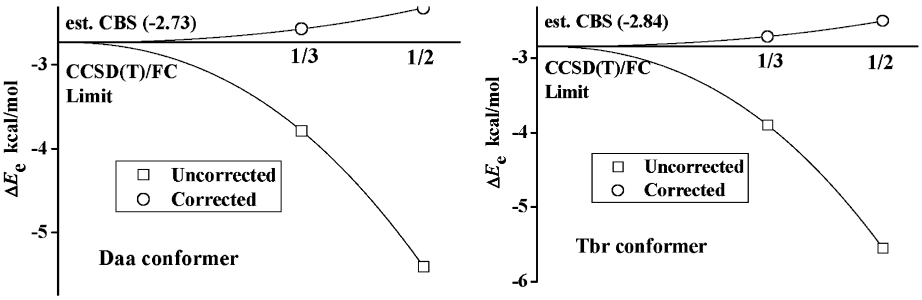

Figure 3. CCSD(T)/CBS limit binding energies for conformers Daa and Tbr.

are nearly flat. On a similar note, the rotation of the facial benzene is facile in the stacked conformation.

At the RI-MP2/CBS level, Dbr is a global minimum (D_e = 5.03 kcal/mol) and Tat is a local minimum (D_e = 3.84 kcal/mol). Thus, the displaced-stacked conformers of Daa/Dab/Dbr are ~1.2 kcal/mol lower in energy than the T-shaped conformers of Tar/Tbr/Tat. On the other hand, CCSD(T)/CBS predicts that Tbr/Tar/Tat (D_e = 2.84 kcal/mol) are ~0.1 kcal/mol lower than Daa/Dab/Dbr (D_e = 2.73 kcal/mol). Because CCSD(T) results are considered to be much more reliable than MP2 results, our discussion will be based on the CCSD(T) results. Then, Tbr/Tar/Tat would be slightly more stable, or at least both Tbr/Tar/Tat and Daa/Dab/Dbr would be nearly equally stable. The potential surface has two flat minima composed of isoenergetic configurations, and the barrier between the two minima is very small (~0.1 kcal/mol). This results in an extremely floppy structure that encompasses diverse configurations with quantum statistical distribution, similar to what is noted in the benzene−water dimer.[45] It is interesting to note that a recent study based on DFT-SAPT calculations with optimized functionals by Podeszwa and Szalewicz[17] yields energies that are in good agreement with the CCSD(T)/CBS results. This seems to indicate that the DFT-SAPT employing optimized functionals would be a promising approach to yield reliable interaction energies for π-containing systems.

The ZPE correction does not significantly alter the energy difference between Tbr and Daa. However, the T-shaped conformer is more flexible (with both rotation and twisting of

TABLE 2: Binding Energies (Calculated/Experimental Values in D_e/D_o in kcal/mol) and Interphenyl Distance (Vertical Distance r_v in Å) [(Center-to-Center Distance r_{cc} in Å)] of the Benzene Dimer

ref	calcd D_e (r_v) [r_{cc}]	S	D	T
this work	est-CCSD(T)/CBS-opt	1.66 (3.89)	2.73 (3.54) [3.95]	2.84 [4.96]
	est-CCSD(T)/CBS//MP2/aVDZ	1.53 (3.75)	2.62 (3.41) [3.74]	2.87 [4.92]
17a	SAPT(DFT)/aVTZ+b	1.85 (3.81)	2.74 (3.46) [3.96]	2.77 [4.95]
14a	est-CCSD(T)/CBS	1.81 (3.9)	2.78 (3.6) [3.94]	2.74 [5.0]
13a	est-CCSD(T)/CBS	1.48 (3.8)	2.48 (3.5) [3.94]	2.46 [5.0]
15c	MP2/6-311+G(2d,p)//MP2/6-311(2d,2p)	2.47 (3.8)	3.79 (3.4) [3.73]	2.87 [5.0]
10d	CCSD(T)/aVDZ	1.12 (4.1)	2.01 (3.6) [4.02]	2.17 [5.1]
17a	{**ΔZPE**}**:** SAPT(DFT)/aVDZ+b[a]		{−0.319}	{−0.315}
this work	{**ΔZPE**}**:** MP2(BSSE)/aVDZ		{−**0.14**}	{−0.26/−**0.25**[b]}
	D_o: est-CCSD(T)/CBS-opt		**2.59**	2.58/**2.59**[b]
ref	exptl D_o [r_{cc}]	S	D	T
8c	D_o			2.4 ± 0.4
8i	D_o			1.6 ± 0.2 (2.1 ± 0.3)[c]
7b	D_o			1.6 ± 0.5
8b	[r_{cc}]			[4.96]

[a] ZPE correction based on only six intermolecular modes (the intramolecular ZPEs were not considered). [b] Because at the MP2(BSSE)/aVDZ level the conformer T has one imaginary frequency (though CCSD(T)/aVDZ indicates that it should be a positive frequency as a global minimum), the six intermolecular frequencies are replaced by the corresponding SAPT(DFT)/aVDZ+b frequencies in that the SAPT(DFT)/aVDZ+b potential reproduces the CCSD(T)/aVDZ potential very well. Thus, this corrected value would be more realistic. [c] See the text.

the axial benzene) and therefore would be more stabilized than the stacked conformer at nonzero temperatures due to the entropic effect. BSSE-corrected MP2/aVDZ frequencies yield ZPE corrections of ∼0.14 kcal/mol for Daa/Dbr, ∼0.21 kcal/mol for Tba, and ∼0.25 kcal/mol for Tar/Tbr/Tat (Table 2). Then, the CCSD(T)/CBS ZPE-corrected dissociation energies ($D_0 = -\Delta E_0$) of both the lowest displaced-stacked conformers (Daa/Dab/Dbr) and the lowest T-shaped conformers (Tar/Tbr/Tat) are isoenergetic (∼2.59 kcal/mol). For a better accuracy, we may need to consider the quadruple excitation effect in the coupled cluster theory. Recently, Hopkins and Tschumper reported the differences in $\pi-\pi$ interaction energies between CCSD(TQ) and CCSD(T) ($\delta_{\mathrm{CCSD(T)}}{}^{\mathrm{CCSD(TQ)}}$) for the T-shaped and stacked dimer conformers of N_2, ethylene, NCCN, butadiene, and furan.[46] We note that $\delta_{\mathrm{CCSD(T)}}{}^{\mathrm{CCSD(TQ)}}$ is correlated to the differences in $\pi-\pi$ interaction energies between CCSD(T) and CCSD ($\delta_{\mathrm{CCSD}}{}^{\mathrm{CCSD(T)}}$), i.e., $\delta_{\mathrm{CCSD(T)}}{}^{\mathrm{CCSD(TQ)}} = -k\delta_{\mathrm{CCSD}}{}^{\mathrm{CCSD(T)}}$, where constant $k \approx 0.173$ with a correlation r factor of 0.85. For the benzene dimer, we find that $\delta_{\mathrm{CCSD}}{}^{\mathrm{CCSD(T)}}$ for Tbr/Daa is −0.74/−1.39 kcal/mol, and so $\delta_{\mathrm{CCSD(T)}}{}^{\mathrm{CCSD(TQ)}}$ for Tbr/Daa is roughly estimated to be 0.13/0.24 kcal/mol. Thus, with this quadruple excitation effect, the accurate D_0 of the benzene dimer would be ∼2.46/2.35 kcal/mol for the T-shaped/displaced-stacked conformer. As the temperature increases, the D_0 of the T-shaped/displaced-stacked conformer decreases (∼2.46/2.35 kcal/mol at 0 K, ∼1.97/1.87 kcal/mol at 30 K, ∼1.60/1.49 kcal/mol at 50 K, and ∼0.77/0.60 kcal/mol at 100 K), and the T-shaped conformer becomes more stable than the displaced-stacked conformer due to the entropic effect. The calculated D_0 value agrees with the experimentally estimated D_0 (at low temperatures) of ∼2 kcal/mol (1.6 ± 0.5,[7b] 2.4 ± 0.4 kcal/mol,[8c] 1.6 ± 0.2 kcal/mol,[8i] or 2.1 ± 0.3 kcal/mol when we assume that the experimental benzene trimer binding energy[8i] is described by three pairs of the benzene dimer interaction). As temperature effects are important in evaluation of binding energies and spectra for clusters,[47] we note that other experimental D_0's (0.7−2 kcal/mol)[7c,d] are also consistent with the theoretical prediction. This clearly demonstrates that the MP2/CBS D_0 (∼5 kcal/mol) is highly overestimated.

The ionization potentials (IP) of Daa/Dab/Dbr and Tar/Tbr/Tat are 8.66 [8.60] and 8.93 [8.87] eV at CCSD(T)/aVDZ [CCSD(T)/aVDZ′]. Because the experimental IP is 8.86 eV,[7b−d] this would correspond to Tar/Tbr/Tat. This indicates that in the gas-phase experiment, the T-shaped structure would preferentially have been observed. Furthermore, the predicted T-shaped structure Tbr(/Tar) having the center-to-center distance (r_{cc}) of 4.96 Å is in excellent agreement with the microwave experiment (4.96 Å),[8b] confirming that the structure is indeed the Tbr/Tar shape. The C−H distance of the axial benzene in Tar/Tbr is slightly shortened by 0.025 Å, showing the blue-shifted C−H frequency by 14 cm^{-1} (based on BSSE-corrected MP2/aVDZ). This result was previously discussed as the blue-shift of the improper H-bond.[48] In a while, the predicted vertical inter-planar distance of the displaced-stacked structure is 3.54 Å, in reasonable agreement with the crystal data of the aromatic systems (3.3−3.7 Å).[3,49]

The SAPT(MP2) interaction energy components [electrostatic energy (E_{es}), effective induction energy ($E_{\mathrm{ind*}} = E_{\mathrm{ind}} + E_{\mathrm{exch-ind}}$), effective dispersion energy ($E_{\mathrm{disp*}} = E_{\mathrm{disp}} + E_{\mathrm{exch-disp}}$), and effective exchange repulsion ($E_{\mathrm{exch*}}$: sum of the first-order perturbation terms)][11] are in Table 3. SAPT/aVDZ′ gives E_{tot} much closer to the CCSD(T)/CBS than SAPT/aVDZ (that overestimates the dispersion energy). As the basis set increases (from 6-31+G* to aVDZ′ to aVDZ), $E_{\mathrm{disp*}}$ significantly increases, and other energy components (E_{es}, $E_{\mathrm{ind*}}$, and $E_{\mathrm{exch*}}$) barely change. In this regard, the total energies can be replaced by the CCSD(T)/CBS total energies ($E_{\mathrm{tot}}{}^{\ddagger}$); the overestimated $E_{\mathrm{disp*}}$ at the MP2 level can be substituted for $E_{\mathrm{disp*}}{}^{\ddagger}$ by correcting as much as the overestimated energy of MP2/aVDZ over CCSD(T)/CBS (Table 3). Then, all the energy components do not significantly depend on the calculation methods. From Table 3, one can easily note that E_{es} [or $E_{\mathrm{es}} + E_{\mathrm{ind*}}$ ($=E_{\mathrm{es+ind*}}$)] is close to the CCSD(T)/CBS total interaction energies ($E_{\mathrm{tot}}{}^{\ddagger}$), and the amount of $E_{\mathrm{disp*+exch*}}{}^{\ddagger}$ ($=E_{\mathrm{disp*}}{}^{\ddagger} + E_{\mathrm{exch*}}$) is rather small. Namely, $E_{\mathrm{disp*}}{}^{\ddagger}$ tends to be mostly cancelled out by $E_{\mathrm{exch*}}$ in the equilibrium structure. It is interesting to note that the values of $E_{\mathrm{disp*+exch*}}{}^{\ddagger}$ for Sab, Daa, and Tba/Tbr/Tat are around −0.5, +1.0, and −0.2 kcal/mol, respectively. For Tba/Tbr/Tat, the effective dispersion energy is (almost) cancelled out by the exchange repulsion. Furthermore, for Daa the smaller magnitude of the dispersion energy as compared to the exchange repulsion leads to a repulsive interaction. Only for Sab (and Saa), is the effective dispersion energy significantly more than the magnitude of the exchange repulsion. However, this energy gain (∼0.5 kcal/mol) is still smaller than E_{es} (∼0.75 kcal/mol). Given that Tba/Tbr/Tat and Daa/Dab are the most stable conformers (more

TABLE 3: SAPT(MP2) Interaction Energy Components (kcal/mol) for Important Conformers of the Benzene Dimer[a]

	aVDZ′					aVDZ				
	Sab	Daa	Tba	Tbr	Tat	Sab	Daa	Tba	Tbr	Tat
E_{tot}	−1.88	−3.01	−2.54	−2.62	−2.63	−3.05	−4.45	−3.29	−3.42	−3.44
$E_{tot}^{‡}$	**−1.53**	**−2.62**	**−2.77**	**−2.84**	**−2.84**	**−1.53**	**−2.62**	**−2.77**	**−2.84**	**−2.84**
E_{es}	**−0.73**	**−2.66**	**−1.99**	**−2.04**	**−2.08**	**−0.75**	**−2.66**	**−1.96**	**−2.02**	**−2.05**
$E_{ind}*$	−0.21	−0.29	−0.24	−0.23	−0.24	−0.22	−0.31	−0.26	−0.25	−0.26
$\delta_{int,resp}^{HF}$	−0.12	−0.61	−0.34	−0.35	−0.36	−0.12	−0.61	−0.35	−0.36	−0.38
$E_{disp}*$	−6.36	−7.96	−4.02	−4.26	−4.36	−7.70	−9.61	−4.83	−5.12	−5.24
$E_{disp}*^{‡}$	−6.01	−7.57	−4.25	−4.48	−4.57	−6.18	−7.78	−4.26	−4.54	−4.64
$E_{exch}*$	5.55	8.51	4.05	4.27	4.41	5.74	8.75	4.12	4.33	4.49
$E_{es+ind*}$	−0.94	−2.96	−2.23	−2.27	−2.32	−0.97	−2.97	−2.22	−2.27	−2.31
$E_{disp*+exch*}$	−0.82	0.56	0.03	0.01	0.05	−1.96	−0.86	−0.71	−0.78	−0.76
$E_{disp*+exch*}^{‡}$	−0.47	0.95	−0.20	−0.21	−0.17	−0.44	0.97	−0.19	−0.20	−0.16

[a] Refer to the text and ref 11 for the notation of energy components. Because the MP2/aVDZ energy is overestimated as compared to the CCSD(T)/aVDZ energy, this difference has been corrected to obtain a more realistic value of E_{tot}(aVDZ) which is marked in "‡". $E_{tot}^{‡}$ is well correlated with E_{es}. The SAPT decompositions with the 6-31+G* basis set are as follows: for Daa and Tba, values of E_{tot}, E_{es}, $E_{ind}*$, $E_{disp}*$, $E_{exch}*$, $E_{disp*+exch*}$, $E_{disp*+exch*}^{‡}$ are −2.07, −2.58, −0.28, −7.03, +8.38, +1.35, +0.80 and −2.09, −2.11, −0.22, −3.43, +3.98, +0.55, −0.13 kcal/mol, respectively.

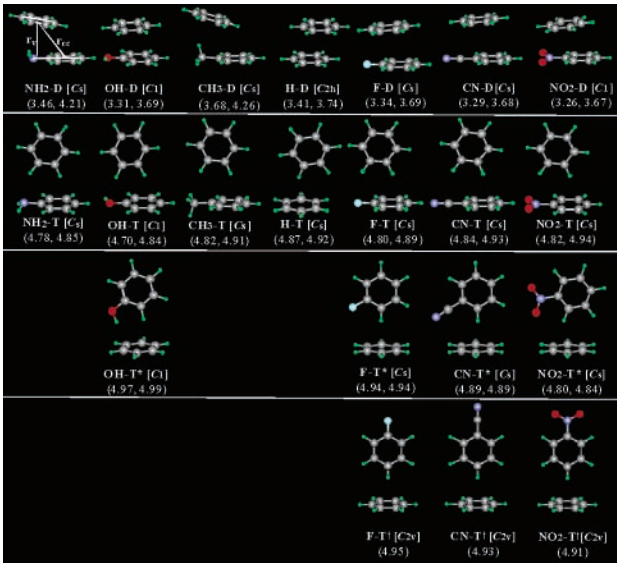

Figure 4. Structures for the substituted benzene−benzene dimer with the BSSE-corrected interphenyl distance geometry optimized at the MP2/aVDZ level. Two numbers (r_v, r_{cc}) in parentheses are the vertical height from the base benzene to the benzene ring center (r_v) and the distance between the two ring centers (r_{cc}) in Å. The molecular symmetry is given in brackets. Missing conformers in the figure (T* and T† for X = NH$_2$/CH$_3$, T† for X = OH) are not stable.

TABLE 4: Interaction Energies (ΔE_e) for Substituted Benzene−Benzene Complexes[a]

	X						
	NH$_2$	OH	CH$_3$	H	F	CN	NO$_2$
			ΔE_0^h: MP2(Full)/6-31+G*				
D	-4.64_0	-4.20_0	-3.96_0	-2.71_0	-3.98_0	-4.96_0	-6.73_0
T	-3.93_1	-3.10_1	-3.03_1	-2.30_1	-2.83_1	-3.02_2	-3.58_3
T*		-4.55_0			-2.78_1	-3.96_1	-4.16_1
T†					-2.54_2	-2.77_2	-2.93_2
			ΔE_e: RI-MP2(FC)/aVTZ				
S	−6.23	−6.07	−5.82	−4.71	−5.55	−7.04	−7.96
T	−4.79	−4.42	−4.13	−3.59	−3.75	−3.93	−3.75
T*		−6.08			−3.88	−5.73	−5.15
T†					−3.62	−4.12	−4.16
			ΔE_e(est): RI-MP2/CBS				
D	−6.49	−6.35	−6.03	−4.93	−5.82	−7.34	−8.32
T	−4.97	−4.60	−4.27	−3.73	−3.92	−4.08	−3.93
T*		−6.32			−4.05	−5.96	−5.39
T†					−3.77	−4.28	−4.35
			ΔE_e: CCSD(T)/aVDZ				
D	−3.72	−2.87	−3.40	−2.06	−2.73	−3.50	−4.17
T	−3.46	−2.92	−2.88	−2.46	−2.62	−2.61	−2.44
T*		−4.42			−2.72	−4.05	−3.56
T†					−2.52	−2.97	−3.01
			ΔE_e(est): CCSD(T)/CBS				
D	**−4.45**	−3.65	**−4.00**	−2.68	**−3.44**	−4.35	**−5.15**
T	−3.95	−3.42	−3.31	**−2.86**	−3.07	−3.04	−2.91
T*		**−5.07**			−3.19	**−4.72**	−4.23
T†					−2.94	−3.45	−3.54

[a] The subscript numbers denote the number of imaginary frequencies of the given structure at the MP2/6-31+G* level. If this number is more than 2, the ZPE corrected energies ΔE_0, are not reliable. Superscript h means 50%-BSSE correction. It is interesting to note that 50%-BSSE-corrected MP2/6-31+G* energies are similar to full-BSSE-corrected MP2/CBS energies, and 50%-BSSE-corrected CCSD(T)/aVDZ′ energies are close to the CCSD(T)/CBS energies.

stable than Saa), the electrostatic energy is much more crucial in governing the configuration of the benzene dimer than the dispersion energy. This is depite the fact that the dispersion energy is the dominant entity.

B. Substituent Benzene Dimers. Figure 4 shows the structures of substituted benzene−benzene complexes (Bz:PhX) using the RI-MP2(Full)/aVDZ optimization followed by the BSSE-corrected interphenyl distance optimization. The complexes include benzene−benzene (X = H), toluene-benzene (X = CH$_3$), phenol−benzene (X = OH), aniline−benzene (X = NH$_2$), and fluorobenzene−benzene (X = F), benzonitrile−benzene (X = CN), and nitrobenzene−benzene (X = NO$_2$). D denotes the displaced-stacked conformer; T, T-shaped conformer with the axial benzene and the facial substituted benzene; T*, T-shaped conformer with the facial benzene and the axial ortho-substituted benzene (with respect to the H atom involving the π-H interaction); T†, T-shaped conformer with the facial benzene and the axial para-substituted benzene (with respect to the H atom involving the π-H interaction). The insets in Figure 4 are given in the order of the electron withdrawing strength NH$_2$ < OH < CH$_3$ < H < F < CN < NO$_2$ in terms of Hammett's substituent constants.[56]

The most stable structure of the benzene dimer is predicted to be the T-shaped conformer at the CCSD(T)/CBS level of theory, though the energy difference from the displaced-stacked conformer is very small and both T-shaped and displaced-stacked conformers are on a very flat potential surface.[10,13−14,17] Table 4 lists the interaction energies (ΔE) based on various calculation results including estimated RI-MP2/CBS and CCSD(T)/CBS. As RI-MP2/CBS tends to stabilize stacked conformers more as compared with T-shaped conformers, it is likely that the CCSD(T)/CBS energies would have the same trend. This

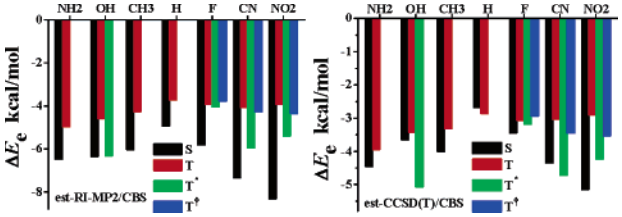

Figure 5. Interaction energies (ΔE_e) for substituted benzene−benzene complexes.

is shown in Figure 5 which compares the interaction energies of all possible types (D, T, T*, and T†) of conformers for the unsubstituted and substituted benzene−benzene complexes at the RI-MP2/CBS and CCSD(T)/CBS levels.

Therefore, we discuss the relative interaction energies of the substituted complexes with respect to the T benzene dimer at the CCSD(T)/CBS levels. Regardless of the electron withdrawing/donating type of substituent, the substituted complex exhibits stronger binding energy ($-\Delta E_e^{\ddagger}$) than the benzene dimer partly because the substituent (NH_2, CH_3, OH, F, CN, and NO_2) in the substituted benzene favorably interacts with the unsubstituted benzene. For the D conformers, the $\delta\Delta E_e^{\ddagger}$ for X = NH_2/OH/CH_3/(H)/F/CN/NO_2 with respect to the D conformer of the benzene dimer is −1.77/−0.96/−1.32/(0)/−0.76/−1.67/−2.47 kcal/mol. These can be contrasted with the corresponding values of the T conformers which are −1.08/−0.55/−0.44/(0)/−0.21/−0.18/−0.04 kcal/mol with respect to the T conformer of the benzene dimer. The stability of T conformers reflects the Hammett constants (σ_p for NH_2/OH/CH_3/H/F/CN/NO_2 is −0.66/−0.37/−0.17/0/+0.06/+0.66/+0.78).[50] In our previous work, when only one H atom in the axial substituted benzene is perpendicularly pointing down to the center of the facial benzene (so-called type I in ref 11), the complexes with an electron withdrawing/donating group are more/less stable than the benzene dimer. This is contrasted to the present T structures where one CH group of the axial benzene points to the π face and the other CH group points to the negative site of the substituent (F/CN/NO_2) of the facial substituted benzene. The T structures have additional electrostatic interactions between the CH group and the substituent negative site, though the energy gain is small. Overall, the energy gain by the substituent effect is greater in the D conformers than in the T conformers.

In Table 4, the D vs T interaction energies (ΔE_e) of the benzene dimer (X = H) by the simple approximation for CCSD(T)/CBS are −2.68 vs −2.86 kcal/mol. These values are well compared with the more accurate values of −2.73 vs −2.84 kcal/mol based on geometry optimization at the estimated CCSD(T)/CBS level in Table 1. The T conformer is only slightly more stable. The D vs T(T*) interaction energies (ΔE_e) for X = NH_2/CH_3/F/NO_2 are −4.46/−4.00/−3.44/−5.15 vs −3.95/−3.31/-3.07(−3.19)/−2.91(−4.23) kcal/mol. For X = OH/CN, the T* conformer (ΔE_e = −5.07/−4.72 kcal/mol) is more stable than the D conformer (ΔE_e = −3.65/−4.35 kcal/mol) because of the strong electrostatic interaction between the substituent (OH/CN) and the facial benzene H/C atom. Then, the interaction energies by the substituent effect are in the order of X = NO_2 (D: −5.15 kcal/mol), X = OH (T*: −5.07 kcal/mol), X = CN (T*/S: −4.72/−4.35 kcal/mol), X = NH_2 (S: −4.45 kcal/mol), X = CH_3 (D: −4.00 kcal/mol), X = F (D: −3.45 kcal/mol), and X = H (T/S: −2.86/−2.68 kcal/mol).

An interesting outcome of the substituent effect is on the displaced-stack vs T-shape (D vs T) stabilization energies. The D vs T stabilization in the benzene dimer can give some implications for the stabilization of protein secondary and tertiary structures and protein folding. Substituted phenyl rings are good models for the side chains of the aromatic amino acids like tyrosine and phenylalanine. Interestingly, these two aromatic side chains have been implicated to play a crucial role in stabilizing the tertiary structure of proteins by linking elements of the secondary structure.[5] The influence of the D vs T competition has been widely discussed in this context, along with the analysis of X-ray data.[5b]

In the study of protein X-ray structures, Rappe and coworkers[5b] found that the aromatic side chains are preferentially aligned in “an off-centered parallel orientation”, denoted as D conformation herein. Furthermore, they were able to extract the relative energy of the D and T conformations and concluded that for phenylalanine the D conformer is 0.5−0.75 kcal/mol more stable than the T conformer. This difference was found to increase to 1 kcal/mol, if other aromatic side chains like tyrosine, histidine, and tryptophan are also considered. Though the X-ray structures are based on free energies, the entropic contributions would be small in crystals; furthermore,these contributions would be similar between different systems, resulting in the cancellation effect on their energy difference. Therefore, the energy differences between D and T conformers in Table 4 could be good approximations of the free energy differences in crystals. This reveals that all substituents, regardless of their nature, stabilize the D conformer more strongly than the T conformer. In the case of benzene−toluene interaction, the D conformer is more stable than the T conformer by 0.69 kcal/mol. Because an additional methyl group in the toluene dimer further enhances the stability of the D conformer (as compared to the benzene−toluene complex), the resulting D/T preference is in good agreement with the Rappe’s estimation[5b] (0.5−0.75 kcal/mol). As will be shown later, the origin of the additional stabilization is largely electrostatic. The electrostatic origin reduces the aromatic interaction strength in polar solvents, as discussed in our previous work.[11] Therefore the D/T preference in terms of stabilization energy reaches its maximum value in apolar environments (such as hydrophobic core of a protein) and decreases with the growing polarity of the surroundings.

In the aromatic interactions, the importance of the dispersion energy has been well discussed.[11,12,14,32] For the decompositions of the interaction energies of D, T, T*, and T†, we carried out SAPT calculations using the aVDZ′ basis set (Table 5). Because the MP2/aVDZ tends to overestimate the interaction energy of the D conformer particularly, the direct comparison between the D and T conformers is not proper. Therefore, as discussed in the benzene dimer, the total interaction energies (E_{tot}) for both MP2/aVDZ and MP2/aVDZ′ need to be replaced by the CCSD(T)/CBS total energies ($E_{tot}^{\ddagger}$). Then, the overestimated E_{disp*} at the MP2 level is also substituted for $E_{disp*}^{\ddagger}$ by correcting as much as the overestimated energy of MP2/aVDZ(′) over CCSD(T)/CBS. Then, again the dependence of the energy components on the calculation level is insignificant.

For the D conformer of the benzene dimer, the total interaction energy ($E_{tot}^{\ddagger}$) is −2.68 kcal/mol, and the electrostatic energy (E_{es}), effective induction energy (E_{ind*}), effective dispersion energy ($E_{disp*}^{\ddagger}$), and effective exchange repulsion (E_{exch*}) are −2.66, −0.29, −7.63, and +8.51 kcal/mol, respectively. For the T conformer of the benzene dimer, $E_{tot}^{\ddagger}$ is −2.86 kcal/mol, and E_{es}, E_{ind*}, $E_{disp*}^{\ddagger}$, and E_{exch*} are −2.04, −0.23, −4.50, and +4.27 kcal/mol, respectively. Overall, the dispersion energy is much more important in the D conformer than the T conformer.

TABLE 5: Substituent Effect (Total and Relative Interaction Energies and Energy Components with Respect to the Benzene Dimer at the MP2/aVDZ′ Level in kcal/mol) for the Aromatic Interactions (D/T/T*/T† Types) by SAPT Decomposition[a]

	type D:X						
	NH_2	OH	CH_3	(H)	F	CN	NO_2
E_{tot}	(−4.70)	(−4.13)	(−4.28)	(−3.01)	(−3.68)	(−4.90)	(−5.72)
E_{es}	(−5.16)	(−4.16)	(−3.75)	(−2.66)	(−3.62)	(−4.95)	(−6.03)
δE_{tot}	−1.69	−1.12	−1.27	(−3.01)	−0.67	−1.89	−2.70
$\delta E_{tot}^{‡}$	**−1.77**	**−0.96**	**−1.32**	**(−2.68)**	**−0.76**	**−1.67**	**−2.47**
δE_{es}	**−2.50**	**−1.50**	**−1.09**	**(−2.66)**	**−0.96**	**−2.29**	**−3.37**
$\delta E_{ind}*$	−0.25	−0.12	−0.11	(−0.29)	0.05	−0.06	−0.10
$\delta\delta_{resp}^{HF}$	−0.13	−0.14	0.01	(−0.61)	−0.08	−0.20	−0.27
$\delta E_{disp}*$	−0.56	−1.23	−0.11	(−7.96)	−0.56	−2.35	−3.29
$\delta E_{disp}*^{‡}$	−0.64	−1.07	−0.16	(−7.63)	−0.65	−2.13	−3.06
$\delta E_{exch}*$	1.75	1.87	0.03	(8.51)	0.88	3.01	4.32
$\delta E_{disp*+exch*}^{‡}$	1.11	0.8	−0.13	(0.88)	0.23	0.88	1.26

	type T:X						
	NH_2	OH	CH_3	(H)	F	CN	NO_2
E_{tot}	(−3.64)	(−3.26)	(−3.06)	(−2.62)	(−2.63)	(−2.83)	(−2.59)
E_{es}	(−3.38)	(−2.79)	(−2.23)	(−2.04)	(−2.09)	(−1.96)	(−1.53)
δE_{tot}	−1.02	−0.64	−0.44	(−2.62)	−0.01	−0.21	0.03
$\delta E_{tot}^{‡}$	**−1.08**	**−0.55**	**−0.44**	**(−2.86)**	**−0.21**	**−0.18**	**−0.04**
δE_{es}	**−1.34**	**−0.75**	**−0.19**	**(−2.04)**	**−0.05**	**0.08**	**0.51**
$\delta E_{ind}*$	−0.17	−0.01	−0.03	(−0.23)	0.06	0.05	0.05
$\delta\delta_{resp}^{HF}$	−0.12	−0.03	−0.03	(−0.35)	0.05	0.06	0.09
$\delta E_{disp}*$	−1.09	−0.71	−0.72	(−4.26)	−0.11	−0.57	−0.64
$\delta E_{disp}*^{‡}$	−1.15	−0.62	−0.72	(−4.50)	−0.31	−0.54	−0.71
$\delta E_{exch}*$	1.69	0.87	0.53	(4.27)	0.04	0.17	0.02
$\delta E_{disp*+exch*}^{‡}$	0.54	0.25	−0.19	(−0.23)	−0.27	−0.37	−0.69

	T*/T†:X						
	T*:OH	T*:F	T*:CN	T*:NO_2	T†:F	T†:CN	T†:NO_2
E_{tot}	(−4.57)	(−2.90)	(−4.45)	(−3.99)	(−2.73)	(−3.20)	(−3.30)
E_{es}	(−4.62)	(−2.37)	(−3.89)	(−3.22)	(−2.16)	(−2.53)	(−2.68)
δE_{tot}	−1.95	−0.28	−1.83	−1.37	−0.11	−0.58	−0.68
$\delta E_{tot}^{‡}$	**−2.21**	**−0.32**	**−1.86**	**−1.37**	**−0.08**	**−0.59**	**−0.68**
δE_{es}	**−2.58**	**−0.33**	**−1.85**	**−1.18**	**−0.12**	**−0.49**	**−0.64**
$\delta E_{ind}*$	−0.87	−0.11	−0.47	−0.39	−0.04	−0.14	−0.19
δd_{resp}^{HF}	−0.50	−0.06	−0.26	−0.28	−0.01	−0.08	−0.12
$\delta E_{disp}*$	−1.02	0.05	−1.53	−1.66	0.22	0.07	−0.06
$\delta E_{disp}*^{‡}$	−1.28	0.01	−1.56	−1.66	0.25	0.06	−0.06
$\delta E_{exch}*$	3.02	0.18	2.28	2.15	−0.17	0.05	0.33
$\delta E_{disp*+exch*}^{‡}$	1.74	0.19	0.72	0.49	0.08	0.11	0.27

[a] The values in parentheses are the total energies and total energy components, whereas otherwise they are the relative energies and relative energy components. $\delta E_{tot}^{‡}$ is the CCSD(T)/CBS energy, which is similar to the BSSE-corrected MP2/aVDZ′ total interaction energy. $E_{tot}^{‡}$ is well correlated with E_{es}.

However, it is interesting to note that $E_{disp*}^{‡}$ is mostly cancelled out by E_{exch*} at their equilibrium geometries where the dominant energy components are dispersion and exchange repulsion. Because of this cancellation effect, though the dispersion is the dominant term, its actual effect is rather small. For all the D, T, and T*/T† conformers, E_{tot} is consistent with and similar to E_{es} ($E_{tot} \approx E_{es}$), but not consistent with E_{exch*}, E_{ind*}, and $E_{disp*}^{‡}$. Further, the analysis of the relative interaction energy and the energy components (δE_{tot}, δE_{es}, δE_{exch*}, δE_{ind*}, $\delta E_{disp*}^{‡}$) with respect to the D-type benzene dimer indicates that $\delta E_{tot}^{‡} \approx \delta E_{es}$ and δE_{exch*} tends to be mostly cancelled out mainly by $\delta E_{disp*}^{‡}$ and partly by δE_{ind*} and the higher order coupled Hartree−Fock response term δ_{resp}^{HF}. Overall, the relative energy of the substitituted benzene complexes is governed mainly by the electrostatic energy except for the conformer T with the NO_2 substitution for which both electrostatic and dispersion are almost equally important (possibly due to the high π-delocation of the NO_2 group).

IV. Insight into Molecular Assembling and Engineering

We here briefly discuss the three examples (Figure 1) mentioned in Introduction.

As a competing force against the $\pi-\pi$ interactions, the hydrogen bond interactions are often used to design nanomaterials, and in particular, organic nanotubes, because these nanotubes have potential applications as artificial biological channels, drug delivery systems, nanochemical reactors, etc. As the strength of 1-D short H-bonding interaction (∼9 kcal/mol,[51] much larger than the typical H-bond interaction of ∼5 kcal/mol of the water dimer[52]) is stronger than the strength of the $\pi-\pi$ displaced-stacking interaction in calix[4]hydroquinone (CHQ) organic nanotubes, the assembling along the 1-D short H-bond relay is much more favorable. However, it should be noted that in this CHQ systems, the $\pi-\pi$ displaced stacking interactions corresponding to the trisubstituted π dimeric sytems would be not small. This, in turn, forms bundles with intertubular $\pi-\pi$ displaced-stacking interactions, resulting in crystals with well-ordered 2-D arrays of pores. A nanotube bundle exhibits well-ordered intertubular $\pi-\pi$ displaced-stacking pairs (Figure 6). Thus, the CHQ tubes assemble to form long tubular structures.[3a]

As graphenes involve in $\pi-\pi$ interactions between adjacent layers, the layer-by-layer peel-off process is possible because of its smooth potential surface. Similarly, multiwalled carbon nanotubes (MWNTs) have cylindrical shapes composed of

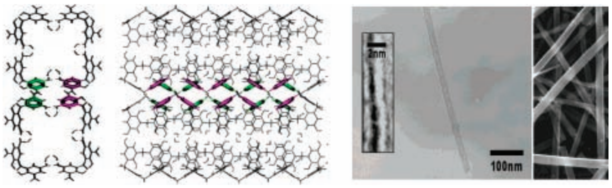

Figure 6. Intertubular $\pi-\pi$ stacking of the CHQ nanotubes and the long tubular structures. (Reproduced by permission of American Chemical Society [ref 3c]).

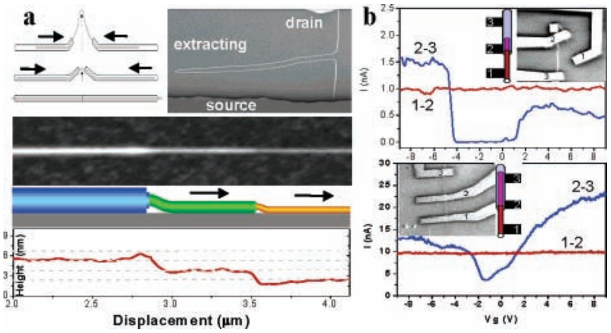

Figure 7. Scanning electron microscope (SEM)/AFM images of a manipulated MWNT formed by moving the AFM tip perpendicular to the nanotube axis (a) and the SEM/AFM images and current−voltage characteristics of the extracted carbon nanotubes (b). In (a), the illustration shows the extraction process that the AFM tip breaks the outermost shells and causes the extrusion of the inner shells of the MWNT by exploiting the nearly flat and frictionless $\pi-\pi$ stacking interactions. An AFM height profile shows the stepwise decrease of the diameter along the extracted nanotube. Each successive structure corresponds to a decrease of the hollowed-out nanotube. In (b), the current is poltted as a function of gate voltage before (blue) and after (red) extraction. The red and blue structures in the schematic represent metallic and semiconducting SWNTs, respectively. The numbers [1,2,3] denote the electrodes. The inset in (b) represents the splitting of a doble-walled nanotube into segments of metallic [1-2] and semiconducting [2-3] SWNTs. The double-walled configuration in (b) [2-3] remains unchanged after extracting the metallic inner-shell [1-2]. Reproduced from ref 28 with permission of the National Academy of Sciences U.S.A. Copyright 2005.

carbon atoms involving in $\pi-\pi$ interactions between neighboring shells. Thus, these nanotubes can be engineered to design electronic devices by extracting the inner shells (Figure 7).[28] The inner shells from MWNTs can be pulled open layer by layer by using an atomic force microscope (AFM). As the $\pi-\pi$ interactions between adjacent shells would be maximized, the displaced-stacked conformations would be frequently present. The resulting interactions would give small barriers for sliding the inner shells in the outer shells. Furthermore, because the inner and outer shells are concentric, the friction would be negligible. This low friction means that the shells will readily telescope out from one another when pulled by the AFM tip. This mechanical inner shell extraction is contrasted with other previous methods such that the inner shells of a MWNT were obtained by removing the outer layers by vaporization or chemical treatment.[53] Using the mechanical approach, we obtain not only hollow outer-shell carbon nanotubes (i.e., nanopipes) but also the very narrow innermost tubes with diameters less than 0.7 nm (down to 0.4 nm), which turned out to be all metallic due to the loss of some of sp^2 character of the carbon atoms.[28]

The strategy for the design and engineering of nanomechanical devices is to harness the subtle changes in the π-electron densities. As an example, quinones are particularly suited for this endeavor because their electronic characteristics can be electrochemically or photochemically controlled. According to a theoretical investigation of the conformational characteristics of *p*-benzoquinone−benzene complexes, the energy difference between the stacked and T-shaped conformations of cyclophane molecules can be substantial. For 2,11-dithio[4,4]-metametaquinocyclophane (MQC), in its neutral state the stacked conformer is 7 kcal/mol more stable than the T-shaped conformer (at the MP2/6-31G* level), whereas in the dianion state the T-shaped conformer is 9 kcal/mol more stable than the stacked conformer. Thus, the subtle control of the conformational characteristics of MQC by electrochemical and/or photochemical means leads to a molecular device. The neutral and dianionic electronic states can be easily transformed into each other by simple electrochemical control of the redox reaction (Figure 8).[29] This would result in large conformational flapping motions. In the presence of solvent molecules, the flapping motion involving squeezing and thrusting by alternating electric field driven electrochemical redox process would be utilized to design a precursor of nanovehicles or nanomechanical devices.

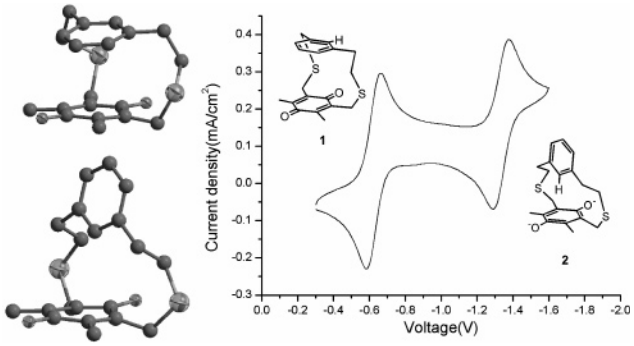

Figure 8. Molecular flipper as a nanomechanical devices: ab initio (MP2/6-31G*) structures of MQC (top left) and the dianionic state (bottom left) and experimental cyclic voltammogram of MQC in acetonitrile (right). Reproduced from ref 29 with permission of the American Chemical Society. Copyright 2002.

V. Conclusion

The aromatic−aromatic interactions are one of the fascinating noncovalent interactions in the sense that the negatively charged and diffuse electron clouds of the π systems exhibit an attractive interaction. In this regard, we investigated the aromatic−aromatic interactions for the T-shaped and stacked conformers of the benzene dimer and variously substituted aromatic systems using ab initio calculations (at the CCSD(T)/CBS level with a least biased extrapolation method). The ZPE-corrected binding energies of both the T-shaped and displaced-stacked conformers of the benzene dimer are estimated to be 2.59 kcal/mol at the BSSE-corrected geometry-optimized CCSD(T)/CBS level. Quadruple excitations in the coupled cluster theory are likely to destabilize the dimer by ~0.13/0.24 kcal/mol. Therefore, the binding energy for T-shaped/displaced-stacked conformers would be ~2.46/2.35 kcal/mol, which is in excellent agreement with experiment. At very low temperatures, both nearly isoenergetic T-shaped and displaced-stacked conformers exhibit quantum statistical distributions for various configurations around their extremely shallow minima, with only a small barrier separating them. However, with increasing temperature, the more flexible T-shaped conformers would be more favored due to the entropy effect. The ionization potential of the T-shaped structure (8.9 eV) is found to be in agreement with the experimental value. The T-shaped structure shows the blue-shifted frequency (14 cm^{-1}) for the π−H interaction mode at the BSSE-corrected potential.

Upon the substitution, the aromatic−aromatic interactions tend to be enhanced regardless of the electron withdrawing and donating groups, as the substituent group also tends to interact with the benzene. This substituent effect is stronger in the displaced-stacked conformers than in the T-shaped conformers. Thus, the cases for X = NO_2, NH_2, CH_3, and F favor the displaced-stacked conformer. The observed prevalence of the displaced-stacked structures among the π-containing organic crystals as well as aromatic side chain interactions in proteins can be explained in terms of the substituent effect (herein, the $-CH_2-$ group in phenylalanine is modeled by a methyl group). The preferential stabilization of the displaced-stacked conformer over the T-shaped conformer by 0.5−0.75 kcal/mol, which was derived from a database study, agrees well with the magnitude of substituent effect estimated in this work. On the other hand, in the case of the T* conformers, the OH and CN groups electrostatically interact with the benzene CH, resulting in enhanced binding energies. The energy difference between the monosubstituted and unsubstituted complexes is as much as up to ∼2.5 kcal/mol (2.5 kcal/mol for the benzen-nitrobenzene and 2.2 kcal/mol for benzene−phenol). This large energy gain should be important in the case of molecular assembly.

The dominant interaction in the aromatic interactions is the dispersion energy, as addressed by Wilcox[26] and theoretically verified by Scherrill.[14] However, the dispersion energy tends to be mostly cancelled out by the exchange repulsion (along with the induction and the higher order response interaction) in the equilibrium geometries of aromatic systems. Therefore, the relative energies depending on different conformations of the aromatic systems and the relative energies between different substitituted benzene complexes are governed mainly by the electrostatic energy, as addressed by Hunter, Sanders, Cozzi, and Siegel,[23,24] and theoretically demonstrated by us.[11] The vital role of the electrostatic energy implies that the substituent effect would be reduced in solution (as was noted experimentally by Wilcox[26]) but is important in apolar media, in particular, for assembling processes. It also supports the experimental observation that in proteins the preference for displaced stacked over T-shaped conformers reaches its maximum value in apolar environments such as hydrophobic core of a protein and decreases with the growing polarity of the surroundings. The present work indicates that understanding of the aromatic interactions is extremely useful for molecular modeling/design involving molecular recognition, assembling, and engineering and for explaining some of the recent experimental observations on nanomaterials and molecular devices.

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