How Different Are Aromatic π Interactions from Aliphatic π Interactions and Non-π Stacking Interactions?

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S *Supporting Information*

ABSTRACT: We compare aromatic π interactions with aliphatic π interactions of double- and triple-bonded π systems and non-π stacking interactions of single-bonded σ systems. The model dimer systems of acetylene $(C_2H_2)_2$, ethylene $(C_2H_4)_2$, ethane $(C_2H_6)_2$, benzene $(C_6H_6)_2$, and cyclohexane $(C_6H_{12})_2$ are investigated. The ethylene dimer has large dispersion energy, while the acetylene dimer has strong electrostatic energy. The aromatic π interactions are strong with particularly large dispersion and electrostatic energies, which would explain why aromatic compounds are frequently found in crystal packing and molecular self-engineering. It should be noted that the difference in binding energy between the benzene dimer (aromatic–aromatic interactions) and the cyclohexane dimer (aliphatic–aliphatic interactions) is not properly described in most density functionals.

Given that the interactions involved in π systems[1-5] are very important in molecular/biomolecular recognition,[6-9] assembly,[10-12] and engineering,[13,14] there have been numerous studies on π interactions.[15-53] One might speculate if there are significant differences in dispersion energies between aromatic π interactions and aliphatic π interactions[54] or non-π stacking interactions and between single, double, and triple-bonded π systems. In this regard, it is necessary to compare the inter-molecular interaction energies for dimers of acetylene HC≡CH (triple bond; t-), ethylene H_2C=CH_2 (double bond; d-), ethane H_3C—CH_3 (single bond; s-), benzene $(\ddot{C}H\ddot{C}H—)_3$ (aromatic bond; a-), and cyclohexane $(—CH_2—CH_2—)_3$ (cyclic single bond; h-). To this end, we need to focus our attention on the dimerization energy at high levels of theory and its energy decomposition. Since the dispersion energy is very important in π interactions, this study requires the complete basis set (CBS) limit binding energies at the level of coupled cluster theory with single, double, and perturbative triple excitations [CCSD(T)]. The strength of the π-interactions is determined by the combined effect of attractive forces (electrostatic, dispersive, and inductive) and repulsive forces (electrostatic, exchange repulsion). Each of these components shows distinctive differences in physical origin, magnitude, and directionality of the molecular interaction. This investigation is done by using symmetry adapted perturbation theory (SAPT) calculations. On the basis of the above calculations, we show the importance of aromatic π interactions in crystal packing and molecular self-engineering. In addition, since all of these results are very useful to test the reliability of various functionals for density functional theory (DFT), their validity for π-interactions along with their strength and weakness is assessed.

To search for the lowest energy structures of acetylene, ethylene, ethane, benzene, and cyclohexane dimers, we investigated diverse topologically different conformers using a few different types of DFT calculations. To confirm the minimum energy structures for the acetylene, ethylene, and ethane dimers,
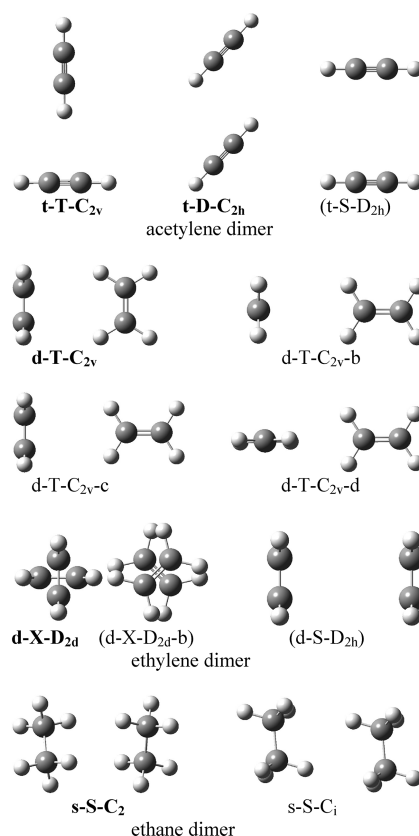

Figure 1. Low energy structures of the acetylene(t-) dimer, the ethylene(d-) dimer, and the ethane(s-) dimer; (t-, triple bonded; d-, double bonded; s-, single bonded).

frequency calculations were carried out at the DFT and Moller—Plesset second order perturbation (MP2) theory levels. Then, the low-lying energy structures were optimized with the basis set superposition error (BSSE) correction at the MP2 level using the aug-cc-pVDZ (aVDZ) and aug-cc-pVTZ (aVTZ) basis
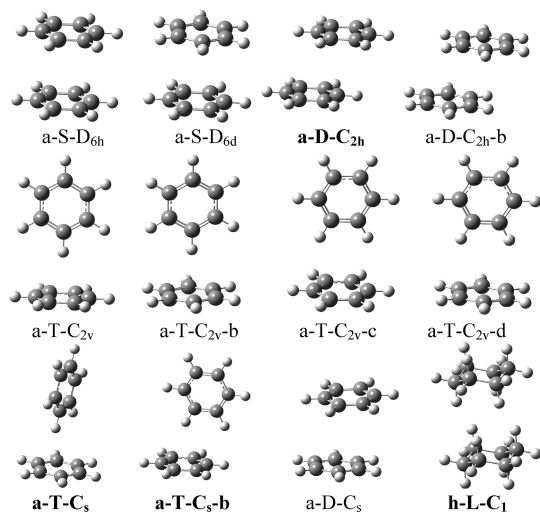

Figure 2. Low energy structures of the benzene(a-) dimer and the cyclohexane(h-) dimer (a-, aromatic bonded; h-, cyclohexane single bonded).

sets for the acetylene, ethylene, and ethane dimers and at the resolution of identity approximation (RI) of MP2 (RI-MP2)/ aVDZ level for the benzene and cyclohexane dimers. Single-point MP2/aug-cc-pVQZ(aVQZ) calculations were performed to estimate the CBS limit binding energies. The estimated CBS limit values were evaluated on the basis of the extrapolation method exploiting the fact that the basis set error in the electron correlation energy is proportional to N^{-3} for the aug-cc-pVNZ (aVNZ) basis set ($E_{CBS} = [E_N*N^3 - E_{N-1}(N - 1)^3]/[N^3 - (N - 1)^3])$.[55,56] We also carried out CCSD(T)/aVDZ optimization and single point BSSE-corrected CCSD(T)/aVDZ and CCSD(T)/aVTZ calculations on the CCSD(T)/aVDZ geometries. However, in the case of cyclohexane dimer, we carried out the same calculations on the BSSE-corrected MP2/aVDZ (RIMP2) geometries. Given that the difference in binding energy between MP2/aVNZ and CCSD(T)/aVNZ does not change significantly with increasing basis set size, we obtained the estimated CCSD(T)/CBS energies by assuming that the difference in binding energies between MP2/aVDZ and MP2/CBS calculations is similar to that between CCSD(T)/aVDZ and CCSD(T)/CBS calculations ($E_{CCSD(T)/CBS} = E_{CCSD(T)/aVDZ} + (E_{MP2/CBS} - E_{MP2/aVDZ})$).[56−58] However, the CCSD(T)/CBS values are also obtained from the extrapolation based on the CCSD(T)/aVDZ and CCSD(T)/aVTZ values. Since the MP2 dispersion energy corrections are not so reliable, the latter extrapolation method could be a better choice. The BLYP/ TZVP, B97-D/TZVP,[59] B3LYP-D/aVTZ,[60] BLYP-D3/TZVPP,

Table 1. DFT, MP2/CBS, and CCSD(T)/CBS Binding Energies (-ΔE_e in kcal/mol) for Low Energy Structures of the Triple-Bonded Acetylene (t-), Double-Bonded Ethylene (d-), Single-Bonded Ethane (s-), Aromatic-Bonded Benzene (a-) and Cyclic Single-Bonded Cyclohexane (h-) Dimers[a]

	M06-2X/aVDZ	M06-2X/DIDZ	MPWB1K/aVDZ	BLYP/TZVP	B97-D/TZV2P	B3LYP-D/aVTZ	MP2/CBS	CCSD(T) /CBS[b]
t-D-C_{2h}	1.57(+0.20)	1.31(−0.06)	1.13(−0.24)	1.31(−0.6)	1.39(**+0.02**)	1.44(+0.07)	1.51(+0.14)	1.37[1.33]
t-T-C_{2v}	1.68(**+0.13**)	1.49(−0.06)	1.37(−**0.18**)	1.65(+0.10)	1.70(+0.15)	1.79(+0.24)	1.63(+0.08)	1.55[1.45]
d-X-D_{2d}	2.13(+0.73)	1.63(+0.23)	1.12(−0.28)	1.65(+0.25)	1.57(+0.17)	1.98(+0.58)	1.54(+0.14)	1.40[1.41]
d-T-C_{2v}	1.34(+0.36)	1.07(+0.09)	0.57(−0.41)	1.13(+0.15)	1.18(+0.20)	1.24(+0.26)	1.25(+0.27)	0.98[1.00]
s-S-C_2	2.25(+0.82)	1.61(+0.18)	0.90(−0.53)	1.71(+0.28)	1.57(+0.14)	2.09(+0.62)	1.37(**+0.06**)	1.43[1.33]
a-D-C_{2h}	3.96(**+1.23**)	3.09(**+0.36**)	1.90(−0.83)	2.33(−0.40)	2.78(+0.05)	2.50(−0.23)	4.93(**+2.18**)	2.73[2.66]
a-T-C_s	3.59(+0.75)	2.90(+0.06)	1.58(−1.26)	2.89(+0.05)	3.08(+0.24)	3.12(+0.28)	3.72(+0.88)	2.84[2.81]
h-L-C_1	3.30(+0.68)	2.21(−0.41)	1.02(−**1.60**)	4.15(**+1.53**)	3.98(**+1.36**)	4.38(**+1.76**)	2.76(+0.14)	[2.62]
MAD[c]	0.61	0.18	0.67	0.42	0.29	0.50	0.48	

	BLYP-D3/TZVPP	PBE-D3/TZVPP	TPSS/LP	wB97XD/aVDZ	wB97XD/6-311+G**	M06HF/aVDZ	M06HF/MG3S
t-D-C_{2h}	1.35(−0.02)	1.63(+0.26)	1.43(+0.06)	1.70(+0.33)	1.59(+0.22)	1.55(+0.18)	1.39(+0.02)
t-T-C_{2v}	1.58(+0.03)	1.59(+0.04)	1.54(−0.01)	1.85(**+0.30**)	1.64(**+0.09**)	1.76(+0.21)	1.32(−0.23)
d-X-D_{2d}	1.47(+0.07)	1.61(+0.21)	1.82(+0.42)	2.12(+0.70)	1.90(+0.50)	1.59(+0.19)	1.33(−0.07)
d-T-C_{2v}	1.13(+0.15)	1.44(+0.46)	1.19(+0.21)	1.52(+0.54)	1.41(+0.43)	1.19(+0.21)	0.83(−0.15)
s-S-C_2	1.24(−0.19)	1.25(−0.18)	1.90(+0.47)	2.34(+0.91)	2.02(+0.59)	1.56(+0.13)	1.05(−0.38)
a-D-C_{2h}	2.49(−0.24)	2.51(−0.22)	3.38(+0.65)	4.42(+1.69)	4.10(+1.37)	4.42(**+1.69**)	3.39(**+0.66**)
a-T-C_s	2.42(−**0.42**)	2.38(−0.46)	2.79(−**0.05**)	3.99(+1.15)	3.66(+0.82)	4.11(+1.27)	2.94(+0.10)
h-L-C_1	2.95(**+0.33**)	3.22(**+0.60**)	3.75(**+1.13**)	4.99(**+2.37**)	4.51(**+1.89**)	2.10(−**0.52**)	1.57(−**1.05**)
MAD[c]	0.18	0.30	0.38	1.00	0.74	0.55	0.33

[a] While the geometries for MP2/CBS and CCSD(T)/CBS were optimized at the MP2/aVDZ and CCSD(T)/aVDZ levels of theory, respectively, those for all other methods were optimized at each given calculation method. For the CCSD(T)/CBS value of the cyclohexane dimer, the intermolecular distance of the MP2/aVDZ optimized geometry was optimized at the CCSD(T)/aVDZ level. The values in parentheses are the differences of the theoretical method-dependent binding energies from the CCSD(T)/CBS values. The bold characters indicate the largest upper and the smallest lower binding energy differences with respect to the CCSD(T)/CBS values. [b] CCSD(T)/CBS values are obtained from the extrapolation by using the CCSD(T)/aVDZ and CCSD(T)/aVTZ values. In the brackets, the values are obtained by assuming that the difference in binding energies between MP2/aVDZ and MP2/CBS calculations is similar to that between CCSD(T)/aVDZ and CCSD(T)/CBS calculations.[56−58] Since the MP2 dispersion energy corrections are not so reliable, the former extrapolation method could be a better choice. [c] MAD is mean absolute deviation.

3472

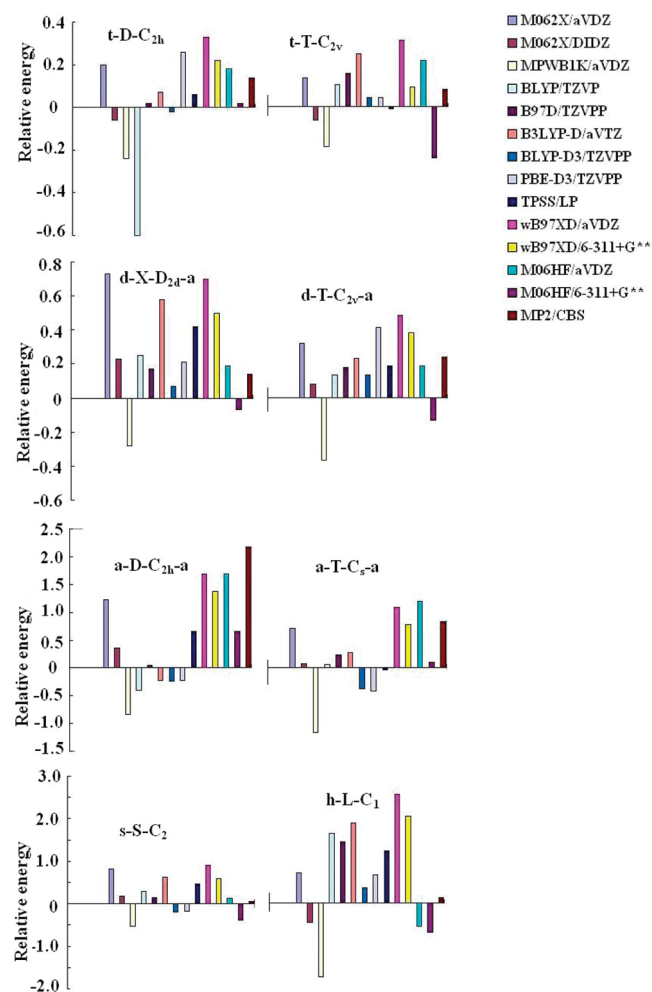dx.doi.org/10.1021/ct200586g |*J. Chem. Theory Comput.* 2011, 7, 3471–3477

Figure 3. Difference of the binding energies of DFT and MP2/CBS from the CCSD(T)/CBS values.

PBE-D3/TZVPP, and TPSS/LP calculations were performed with the Turbomol 5.10 suite of programs.[61] In the case of the TPSS functional, we used the 6-311++G**(3df,3dp) basis set (which will be abbreviated as Large Pople's (LP) basis set) because the empirical dispersion is specially parametrized for this particular basis set. The suitable basis set for M06-2X method is the DIDZ basis set in that the results are basis set dependent. The M06-2X,[62] MPWB1K,[63] wB97XD, M06HF, and MP2 calculations were carried out with the Gaussian 09 suite of programs.[64] The CCSD(T) calculations were done with the MOLPRO suite.[65] The molecular structures were drawn with the POSMOL package.[66]

By using SAPT calculations,[67−76] the total interaction energy (E_{tot}) is decomposed into electrostatic (E_{es}), effective induction (E_{in}), effective dispersion (E_{dp}), and effective exchange repulsion (E_x) energies, as in our earlier work[77,78] and others.[67−76] Here, E_{in} and E_{dp} include the exchange-induction term and exchange-dispersion term, respectively, while E_x excludes these terms from the exchange term. The coupled Hartree−Fock response term ($\delta_{int,resp}^{HF}$) is added to E_{in}, since it tends to be more related to the induction than other terms. DFT-SAPT calculations were performed with the PBE0 functional[79] and aVDZ basis set.

Using the DFT level of theory, we investigated many low-energy structures for each dimer. Then, important low-energy structures (Figures 1 and 2) were further investigated by using

MP2 and CCSD(T) calculations. The dimers are named as "group-shape-sym-index". Here, "group" denoted as "s/d/t/a/h" indicates "single/double/triple/aromatic/cyclohexane-single"-bonded; "type" as "S/D/X/T/L" indicates "stacked/displaced-stacked/cross-stacked/T-shaped/overlayered"; "sym" denotes the point group symmetry of molecular cluster; "index" as "/b/c..." distinguishes each isomer from the lowest energy structure for more than two isomers. The predicted binding energies for the important dimer structures at various DFT, MP2/CBS, and CCSD(T)/CBS levels are in Table 1. The binding energies in the literature are reported in Table S5, Supporting Information and the differences in binding energies of DFT and MP2/CBS from the CCSD(T)/CBS values are in Figure 3. Our discussion will be based on the CCSD(T)/CBS results unless otherwise specified, because these results are considered to be very reliable.

First, we briefly discuss the most stable structures of acetylene, ethylene, ethane, benzene, and cyclohexane and their competing stable structures. Although the geometrical search was carried out using various DFT and MP2 methods, these results are not quite consistent with the CCSD(T) results. Thus, we discuss the low energy conformers on the basis of the CCSD(T) results, and then the assessment of other methods will be given in comparison with the CCSD(T) results.

We begin with the discussion on the structures of the various types of dimers in terms of the energies (ΔE_e) on the Born−Oppenheimer potential surface at the level of CCSD(T)/CBS. The most stable stacked structures of acetylene, ethylene, ethane, benzene, and cyclohexane dimers are t-D-C_{2h}, d-X-D_{2d}, s-S-C_2, a-D-C_{2h}, and h-L-C_1, respectively. Against these structures, there are competing stable T-shaped structures of acetylene, ethylene, and benzene, which are t-T-C_{2v}, d-T-C_{2v}, and a-T-C_s, respectively. In most cases, the stacked or displaced-stacked structures are more stable, except for the cases of the acetylene dimer and the benzene dimer for which the T-shaped structures are slightly more stable. In the case of the acetylene dimer, the zero point energy (ZPE) correction makes both t-T-C_{2v} and t-D-C_{2h} nearly isoenergetic, resulting in the quantum probabilistic structure spanning both T-shaped and displaced-stacked structures[80,81] (see the Supporting Information).

Now, we compare various DFT results and MP2 results with the CCSD(T)/CBS results for a few important cases. For the acetylene dimer and the ethylene dimer, the BLYP-D3/TZVPP results are better than other DFT methods. Both BLYP-D3/TZVPP and MP2/CBS results are in reasonable agreement with the CCSD(T)/CBS results. The intermolecular distance between the centers of mass of two ethylene monomers is 3.82 Å at BLYP-D3/TZVPP and MP2/aVTZ, as compared with 3.78 Å at CCSD(T)/aVDZ. Among the DFT methods, BLYP-D3/TZVPP is in good agreement with CCSD(T)/CBS, though slightly overestimated. The MP2/CBS results are also in good agreement with the CCSD(T)/CBS results.

In the case of the benzene dimer, at the DFT level, the displaced-stacked structures are more stable at the M06-2X, MPWB1K, BLYP-D3, PBE-D3, TPSS, wB97XD, and M06HF levels, while the T-shaped isomers are more stable at the BLYP/TZVP, B97-D/TZVP, and B3LYP-D/aVTZ levels. At the MP2/CBS level, the displaced-stacked structure is far more stable than the T-shaped structure, which is the weakest point of the MP2 level of theory on the $\pi−\pi$ interaction.

For the cyclohexane dimer, against the CCSD(T)/CBS binding energy of 2.62 kcal/mol for the isomer h-L-C_1, we note

3473

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Table 2. Center-to-Center Distance of the Low Energy Structures of the Acetylene(t-), Ethylene(d-), Ethane(s-), Benzene(a-), and Cyclohexane(h-) Dimers[a]

	M06-2X/DIDZ	MPWB1K/aVDZ	BLYP/TZVP	B97-D/TZV2P	B3LYP-D/aVTZ	MP2/aVTZ	CCSD(T)/aVDZ	CCSD(T)/aVTZ
				Center-to-Center Distance				
t-D-C_{2h}	4.17(−0.15)	4.27(−0.05)	4.27(−**0.05**)	4.29(−0.03)	4.09(−0.23)	4.18(−0.14)	4.32	4.26
t-T-C_{2v}	4.33(−0.12)	4.42(−0.03)	4.29(−0.16)	4.33(−0.12)	4.27(−**0.18**)	4.35(−0.10)	4.45	4.40
d-X-D_{2d}	3.59(−0.19)	3.84(+0.06)	3.55(−0.23)	3.65(−0.13)	3.51(−0.27)	3.82(+**0.04**)	3.78	3.73
d-T-C_{2v}	3.73(−0.23)	3.86(−0.10)	3.64(−0.32)	3.77(−0.19)	3.63(−0.33)	3.79(−0.17)	3.96	3.91
s-S-C_2	3.52(−**0.33**)	3.73(−**0.12**)	3.46(−0.39)	3.60(−0.25)	3.40(−0.45)	3.70(−0.15)	3.85	3.80
a-D-C_{2h}	3.80(−0.24)	3.92(−0.12)	3.87(−0.17)	3.93(−0.11)	3.84(−0.20)	3.69(−**0.35**)	4.04	3.97
a-T-C_s	4.85(+**0.18**)	5.18(+**0.15**)	4.82(−0.21)	4.87(−0.16)	4.79(−0.24)	4.85(−0.18)	5.03	4.97
h-L-C_1	4.44(−0.18)	4.64(+0.02)	4.20(−**0.42**)	4.26(−0.36)	4.22(−**0.55**)	4.62(−0.15)	4.77	
				Vertical Distance				
t-D-C_{2h}	2.84(−0.09)	2.90(−0.03)	2.90(−**0.03**)	2.90(−**0.03**)	2.79(−**0.14**)	2.77(−0.16)	2.93	2.83
t-T-C_{2v}	2.66(−0.09)	2.75(0.00)	2.62(−0.13)	2.66(−0.09)	2.60(−0.15)	2.68(−0.07)	2.75	2.70
d-X-D_{2d}	1.74(−0.17)	1.99(+0.08)	1.69(−0.22)	1.79(−0.12)	1.66(−0.25)	1.95(+0.04)	1.91	1.86
d-T-C_{2v}	2.85(−0.22)	2.98(−**0.09**)	2.76(−0.31)	2.89(−0.18)	2.76(−0.31)	2.91(−0.16)	3.07	2.98
s-S-C_2	1.76(−**0.31**)	2.00(−0.07)	1.69−0.38)	1.84(−0.23)	1.64(−0.43)	1.94(−0.13)	2.07	2.02
a-D-C_{2h}	3.33(−0.29)	3.57(−0.05)	3.39(−0.23)	3.47(−0.15)	3.37(−0.25)	3.34(−0.28)	3.62	3.56
a-T-C_s	2.49(−**0.08**)	2.74(+**0.17**)	2.46(−0.11)	2.48(−0.09)	2.46(−0.11)	2.42(−0.15)	2.57	2.50
h-L-C_1	1.78(−0.26)	1.99(−0.05)	1.54(−**0.50**)	1.60(−**0.44**)	1.57(−**0.47**)	1.94(−0.10)	2.04	

	BLYP-D3/TZVPP	PBE-D3/TZVPP	TPSS/LP	wB97XD/aVDZ	wB97XD/6-311+G**	M06HF/aVDZ	M06HF/MG3S
			Center-to-Center Distance				
t-D-C_{2h}	4.27(−0.05)	4.27(−0.05)	4.32(0.00)	4.16(−0.16)	4.18(−0.14)	4.14(−0.18)	4.16(−0.16)
t-T-C_{2v}	4.42(−0.03)	4.42(−0.03)	4.52(0.07)	4.34(−**0.11**)	4.38(−**0.07**)	4.35(−0.10)	4.41(−**0.04**)
d-X-D_{2d}	3.82(0.04)	3.82(0.04)	3.73(−0.05)	3.65(−0.13)	3.65(−0.13)	3.71(−**0.07**)	3.65(−0.13)
d-T-C_{2v}	3.80(−0.16)	3.80(−0.16)	3.89(−0.07)	3.74(−0.22)	3.74(−0.22)	3.78(−0.18)	3.89(−0.07)
s-S-C_2	3.67(−0.18)	3.88(0.03)	3.67(−0.18)	3.56(−0.29)	3.59(−0.26)	3.60(−0.25)	3.57(−0.28)
a-D-C_{2h}	3.77(−**0.27**)	3.97(0.07)	3.85(−0.19)	3.82(−0.22)	3.81(−0.23)	3.75(−0.29)	3.74(−**0.30**)
a-T-C_s	5.13(**.10**)	5.18(**.15**)	5.14(**.11**)	4.87(−0.16)	4.89(−0.14)	4.75(−0.28)	4.82(−0.21)
h-L-C_1	4.51(−0.26)	4.59(−0.18)	4.45(−**0.32**)	4.30(−0.47)	4.31(−0.46)	4.47(−**0.30**)	4.51(−0.26)
			Vertical Distance				
t-D-C_{2h}	2.89(−0.04)	2.90(−0.03)	2.90(−0.03)	2.85(−0.08)	2.85(−0.08)	2.77(−0.15)	2.88(−0.05)
t-T-C_{2v}	2.74(−0.01)	2.74(−0.01)	2.85(0.10)	2.66(−0.09)	2.71(−0.04)	2.68(−**0.07**)	2.75(**.00**)
d-X-D_{2d}	1.97(0.06)	1.96(0.05)	1.89(0.02)	1.80(−0.11)	2.73(−0.18)	1.79(−0.12)	1.81(−0.10)
d-T-C_{2v}	2.87(−**0.20**)	2.86(−**0.21**)	2.96(−0.11)	2.80(−0.27)	2.81(−0.26)	2.85(−0.22)	2.97(−0.10)
s-S-C_2	1.94(−0.13)	2.06(−0.01)	1.90(−0.17)	1.80(−0.27)	1.88(−0.19)	2.78(−0.29)	1.83(−0.24)
a-D-C_{2h}	3.43(−0.19)	3.64(0.02)	3.55(−0.07)	3.47(−0.15)	3.45(−0.17)	3.28(−**0.44**)	3.27(−**0.35**)
a-T-C_s	2.80(**.23**)	2.86(**.29**)	2.82(**.25**)	2.54(−0.3)	2.57(**.00**)	2.27(−0.30)	2.42(−0.15)
h-L-C_1	1.85(−0.19)	1.92(0.12)	1.80(−**0.24**)	1.64(−**0.40**)	1.67(−**0.37**)	1.80(−0.24)	1.86(−0.20)

[a] The bold characters indicate the largest upper and the smallest lower distance differences with respect to the CCSD(T)/aVDZ values, which are close to the CCSD(T)/aVTZ values (t-, triple bonded; d-, double bonded; s-, single bonded; a-, aromatic bonded; h-, cyclohexane single bonded).

substantial energy differences between different methods. The binding energy is 1.02 kcal/mol at MPWB1K/TZVPP, 3.30 kcal/mol at M06-2X/aVDZ, 3.98 kcal/mol at B97-D/TZV2P, 4.15 kcal/mol at BLYP/TZVP, 2.95 kcal/mol at BLYP-D3/TZVPP, and 4.38 kcal/mol at B3LYP-D/aVTZ. Among the DFT methods, only the BLYP-D3/TZVPP method gives a reasonable value. The MP2/CBS value (2.76 kcal/mol) is in good agreement with the CCSD(T)/CBS. The intermolecular distance between two centers of mass of the two monomer units is 4.51 Å at BLYP-D3, 4.62 Å at RIMP2/aVTZ, and 4.77 Å at the BBSE-corrected CCSD(T)/aVDZ.

When various DFT and MP2/CBS binding energies are compared with the CCSD(T)/CBS binding energies for t-D-C_{2h}, d-X-D_{2d}, s-S-C_2, a-D-C_{2h}/ a-T-C_s, and h-L-C_1, there are significant discrepancies in certain cases. For example, M06-2X/aVDZ, wB97XD/6-311+G**, wB97XD/aVDZ, and MP2/CBS overestimate the binding energy of a-D-C_{2h} (by 1.2, 1.4, 1.7, and 2.2 kcal/mol, respectively), while MPWB1K/aVDZ underestimates it (by 0.8 kcal/mol). B3LYP-D/aVTZ, BLYP/TZVP, and B97-D/TZV2P overestimate that of a-L-C_1 (by 1.7, 1.5, and 1.3 kcal/mol, respectively), while MPWB1K/aVDZ underestimates it (by 1.6 kcal/mol). The BLYP-D3/TZVPP binding energies

agree with the CCSD(T)/CBS energies within 0.4 kcal/mol, but the a-D-C_{2h}/a-T-C_s is underestimated by 0.2/0.4 kcal/mol, while the h-L-C_1 is overestimated by 0.3 kcal/mol. This results in a substantial binding energy difference (0.75 kcal/mol) between the two cases (i.e., benzene and cyclohexane) as compared with an insignificant binding energy difference between the two (0.1−0.2 kcal/mol) in CCSD(T)/CBS. Among various DFT methods, the M06-2X/DIDZ, B97-D/TZV2P, MP2/CBS, and M06HF/aVDZ methods are better for the ethane dimer. In the case of the T-shaped ethylene dimer, M06-2X/DIDZ, BLYP/TZVP, BLYP-D3/TZVPP, and M06HF/MG3S are better, while for the X-shaped ethylene dimer, MP2/CBS, BLYP-D3/TZVPP, and M06HF/MG3S are better. The M06-2X/DIDZ, BLYP/TZVP, B97-D/TZVPP, BLYP-D3/TZVPP, and TPSS/LP methods are better for the acetylene dimer. The M06-2X/DIDZ, BLYP/TZVP, and TPSS/LP methods are better for the T-shaped benzene dimer, while B97-D/TZVPP is better for the displaced stacked structure. The BLYP-D3/TZVPP and MP2/CBS methods are better for the cyclohexane dimer. Overall, BLYP-D3/TZVPP and M06-2X/DIDZ calculations properly reproduce the CCSD(T)/CBS binding energies as compared with other methods. However, we believe that the DFT functionals need to be further improved to describe the difference in binding energy between the benzene dimer and the cyclohexane dimer. M06-2X/DIDZ, BLYP/TZVP, B97-D/TZVPP, and BLYP-D3/TZVPP are working well, except for the cyclohexane dimer. Overall, M06-2X/DIDZ and BLYP-D3/TZVPP are working well. Its mean unsigned relative error or mean absolute deviation (MAD) is 0.18 kcal/mol. Such deviations in the center-to-center distances and vertical distances for the dimer structures (in particular, significantly shortened distances for the cyclohexane dimer) are also noted in the above DFT calculation methods (Table 2).

Table 3. SAPT-DFT Interaction Energy Components (kcal/mol) for Important Conformers of the Acetylene, Ethylene, Ethane, Benzene, and Cyclohexane Dimers[a]

	t-D-C_{2h}	t-T-C_{2v}	d-X-D_{2d}	d-T-C_{2v}	s-S-C_2	a-D-C_{2h}	a-T-C_s	h-L-C_1
E_{tot}	−1.40	−1.56	−1.29	−1.03	−1.08	−2.67	−2.51	−2.32
E_{es}	−1.82	−2.22	−1.18	−1.04	−0.84	−2.64	−1.99	−1.27
E_{id}	−0.36	−0.72	−0.23	−0.38	−0.19	−0.89	−0.60	−0.38
E_{dp}	−1.52	−1.65	−2.56	−2.41	−3.17	−8.68	−5.01	−5.54
E_x	2.30	3.04	2.68	2.81	3.13	9.54	5.09	4.88

[a] PBE0 functional and aVDZ basis set are employed (t-, triple bonded; d-, double bonded; s-, single bonded; a-, aromatic bonded; h-, cyclohexane single bonded).

The energy components based on the SAPT/DFT are listed in Tables 3 and 4. The total interaction energies for the stacked structures of acetylene, ethylene, ethane, benzene(displaced-stacked/T-shaped), and cyclohexane dimers are −1.40, −1.29, −1.08, −2.67/−2.51, and −2.32 kcal/mol, respectively. As compared with the CCSD(T)/CBS energies, the SAPT/DFT energies of the T-shaped benzene dimer and the cyclohexane dimer are somewhat underestimated by 0.3 kcal/mol, while other cases are close to the CCSD(T) energies. The corresponding E_{dp} values of the above dimers are −1.52, −2.56, −3.17, −8.68/−5.01, and −5.54 kcal/mol, respectively, and the corresponding electrostatic energies (E_{es}) are −1.82, −1.18. −0.84, −2.64/−1.99, and −1.27 kcal/mol, respectively. Although the total interaction energies for acetylene, ethylene, and ethane dimers are similar, the C≡C has much weaker dispersion energy than the C=C, which is again weaker than the C−C (for which the dispersion would arise from the interaction between C and H). On the other hand, the electrostatic energy is large for the acetylene dimer (because of significantly positive charge of H atoms in acetylene, q_H: 0.225 au) but small for the ethane dimer (Figure 4). Again, although the total interaction energies of the dimers for benzene and cyclohexane are similar, the $(\text{\"C\"C\"})_{cyclic}$ case has much stronger dispersion and electrostatic energies than the $(-C-C-)_{cyclic}$ case. Despite that the dispersion energy tends to be correlated with the number of valence electrons participating in the interaction between the molecules (acetylene, 20; ethylene, 22; ethane, 24; benzene, 60; cyclohexane, 66), one can note that the stacked ethane dimer and the displaced-stacked benzene dimer show particularly large dispersion energies. In the case of the benzene dimer, the electrostatic interaction energy (due to the quadrupole moments of benzene) is also large. This result would thus explain why aromatic compounds are easily found in crystals and self-assembled systems.

To obtain insight into these noncovalent interactions, the second order perturbation theory approximately gives the dispersion energies between two 1s electrons (1s−1s), between two 2s electrons (2s−2s), between two $2p_z$ electrons ($2p_z$−$2p_z$), and between $2p_1$ electrons ($2p_1$−$2p_1$) for two hydrogenic atoms, which are separated by distance R along the z axis. These four values in units of $(e^4/R^6)(a_o/Z_{eff})^4$ are estimated to be ∼6 (1s−1s), ∼1176 (2s−2s), ∼1368 ($2p_z$−$2p_z$), and ∼432 ($2p_1$−$2p_1$), where e is the electron charge, a_o is 1 Bohr, and Z_{eff} is the effective nuclear charge of the hydrogenic atom (Z_{eff} is 1 for H, 3.22 for C(2s), and 3.14 for C(2p)). The dispersion energy between 1s(H) and 2s(C) electrons is estimated to be ∼84 $(e^4/R^6)(a_o^4/Z_{eff}^2)$. In general, two closely contacted nonbonded carbon atoms are separated by $R = $∼3.5 Å, while the closely contacted nonbonded distance between H and C is $R = $∼2.5 Å. Then, the C···H dispersion energy is also strong. What is

Table 4. SAPT-DFT Interaction Energy Components (kcal/mol) of the Stacked Conformers of Acetylene, Ethylene, and Benzene Dimers, As in Table 3 (t-, triple bonded; d-, double bonded; s-, single bonded; a-, aromatic bonded; h-, cyclohexane single bonded)

DFT-SAPT	CCSD(T)/aVDZ$_{opt}$ interplane distance			interplane distance 3.41 Å			interplane distance 3.7 Å		
	t-S-C_{2h}	d-S-D_{2h}	a-S-D_{6h}	t−S-C_{2h}	d-S-D_{2h}	a-S-D_{6h}	t−S-C_{2h}	d-S-D_{2h}	a-S-D_{6h}
E_{tot}	0.18	0.00	−1.18	1.67	1.31	0.49	0.71	0.36	−1.18
E_{es}	0.42	0.31	−0.46	−0.01	−0.88	−2.91	0.45	−0.03	−0.46
E_{id}	−0.02	−0.06	−0.30	−0.24	−0.33	−0.52	−0.12	−0.17	−0.30
E_{dp}	−0.33	−0.89	−6.70	−2.32	−3.23	−10.74	−1.38	−1.95	−6.70
E_x	0.12	0.63	6.28	4.23	5.75	14.66	1.76	2.51	6.28

3475

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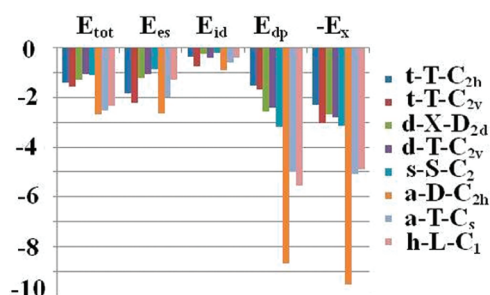
Figure 4. SAPT-DFT/aVDZ energy contributions of the acetylene, ethylene, ethane, benzene, and cyclohexane dimers.

interesting is that the dispersion energy for the $2p_z-2p_z$ electrons is stronger than that for the $2s-2s$ electrons, which is much stronger than that for the $2p_1-2p_1$ electrons. Similarly, in the accurate calculations of the dispersion energy between all electrons of two O atoms, one can note that the van der Waals coefficients of the $3P_1-3P_1$ interaction and the $3P_0-3P_0$ interaction are 18.0 and 16.7 au, respectively.[82] In this regard, we expect that the dispersion energy for $2p_z-2p_z$ electrons would favor the maximally overlapped stacked conformation, while the electrostatic energy would disfavor this overlapping. In the ethene and benzene, the gain by the dispersion energy for $2p_z-2p_z$ electrons is substantial due to their planar conformation, while in the ethane and cyclohexane, the dispersion energy between 1s(H) and 2s(C) electrons is significant. The present results including the competition and cooperation between dispersion and electrostatic energies are very important for investigating the reliability of density functionals in predicting diverse molecular interaction energies.

In summary, we have studied the structural isomers and interaction energy of triple-bonded acetylene, double-bonded ethylene, single-bonded ethane, aromatic benzene, and cyclic single-bonded cyclohexane dimers. In the case of the ethylene dimer, ethane dimer, benzene dimer, and cyclohexane dimer, the dispersion energy is dominant, while in the case of acetylene dimer, the electrostatic energy is dominant. The aromatic π interactions have particularly large dispersion and electrostatic energies among various types of π interactions. This phenomenon would be related to the fact that aromatic compounds are easily found in crystals, which is indeed very important for crystal packing and molecular self-engineering.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Coordinates of the low energy structures at the CCSD(T)/aVDZ level; the various types of DFT, MP2, and CCSD(T) binding energies; previous results in the literature. This material is available free of charge via the Internet at http://pubs.acs.org.

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3476

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