Do Special Noncovalent $\pi - \pi$ Stacking Interaction Really Exist?

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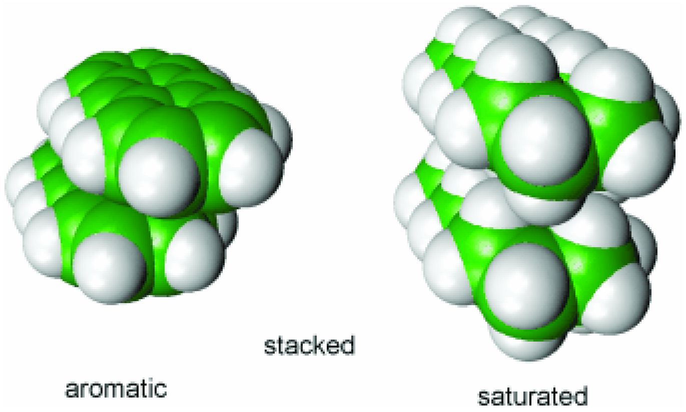
π - π Stacking Effect (PSE)

- The energy difference between stacked aromatic units compared to, for example, saturated (hydrogenated) rings of about the same size.



Before we start……

- Benzene vs.cyclohexane

  both exist as fluids at room temperature.

Similar intermolecular interaction----Incompatible with π - π stacking effect

- Polycyclic aromatic hydrocarbons(PAHs) vs. large alkanes

  PAHs become increasingly insoluble in common solvents with increasing size----

  Compatible with π - π stacking effect

Models

Linear condensed acenes, from benzene to tetracene and their corresponding saturated ring systems.

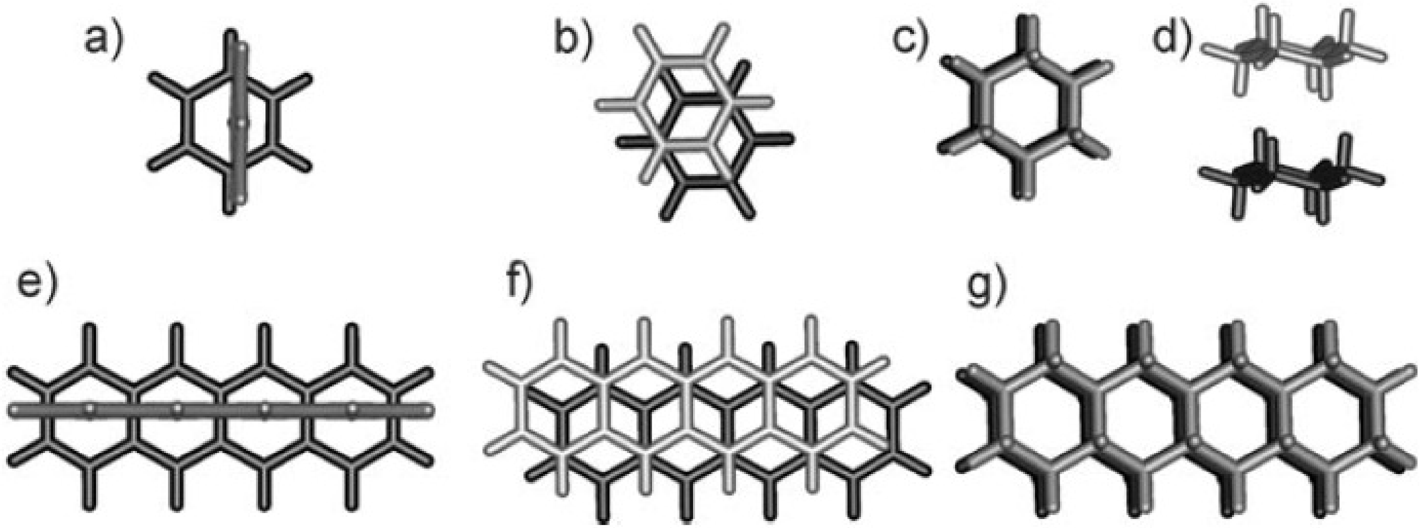


Figure 1. Energy-minimized structures of the benzene dimer: a) T-shaped and b) π–π stacked. c), d) The cyclohexane dimer in two projections. The tetracene dimer: e) T-shaped and f) π–π stacked. g) The octadecahydrotetracene dimer.

Energy-minimized intermolecular distance R

- Saturated series: 426.2—426.5 pm
- Aromatic dimers (PD):

n=1 391.4 [349.4]
n=2 383.0 [337.9]
n=3 379.4 [333.8]
n=4 374.7 [331.4]

decrease

- Aromatic dimers(T-shaped):

n=1 491.3 [493.0]
n=2 493.5 [493.4]
n=3
n=4

The orientation of the monomers also play an important role in $\pi - \pi$ stacking.

Intermolecular interaction energies △E

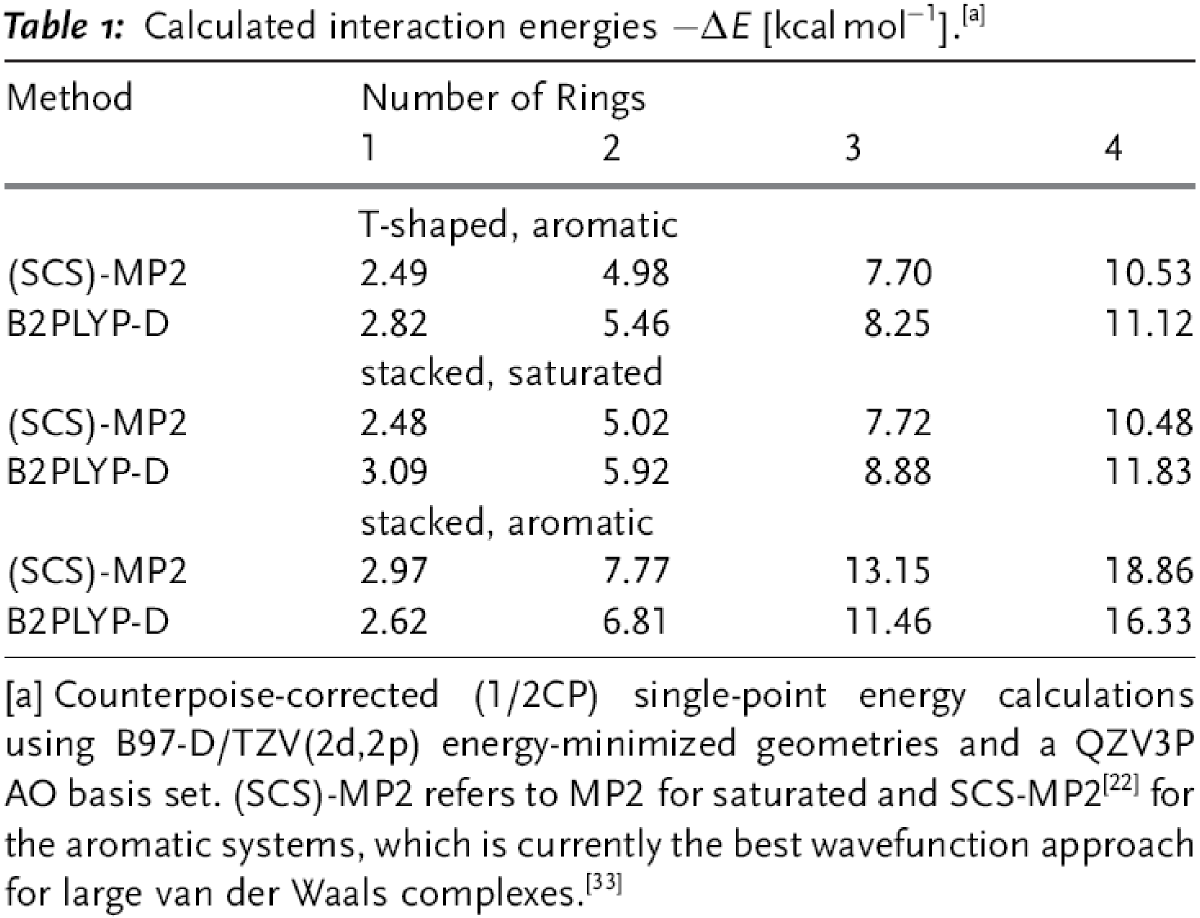


Table 1: Calculated interaction energies $-\Delta E$ [kcal mol^{-1}].[a]

Method	Number of Rings 1	2	3	4
	T-shaped, aromatic			
(SCS)-MP2	2.49	4.98	7.70	10.53
B2PLYP-D	2.82	5.46	8.25	11.12
	stacked, saturated			
(SCS)-MP2	2.48	5.02	7.72	10.48
B2PLYP-D	3.09	5.92	8.88	11.83
	stacked, aromatic			
(SCS)-MP2	2.97	7.77	13.15	18.86
B2PLYP-D	2.62	6.81	11.46	16.33

[a] Counterpoise-corrected (1/2CP) single-point energy calculations using B97-D/TZV(2d,2p) energy-minimized geometries and a QZV3P AO basis set. (SCS)-MP2 refers to MP2 for saturated and SCS-MP2[22] for the aromatic systems, which is currently the best wavefunction approach for large van der Waals complexes.[33]

Do not overestimate the effect of the π System in small size Molecules(<10 C’s).

Intermolecular interaction energies △E

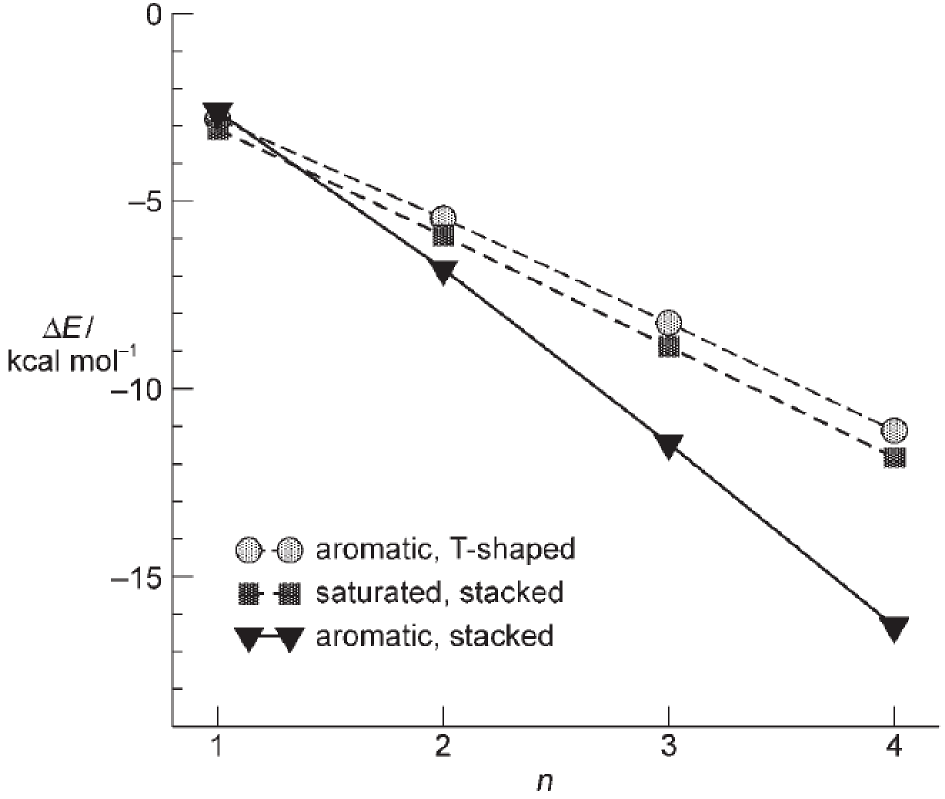


Figure 2. Interaction energies ΔE [B2PLYP-D/QZV3P(1/2CP)] as a function of the number of rings *n*.

The magnitude of the slope Indicates the existence of PSE in stacked aromatic complex.

- There is special interaction in the π - π Stacked arrangement.
- Is the π system directly responsible for it?

Electrostatic Potential

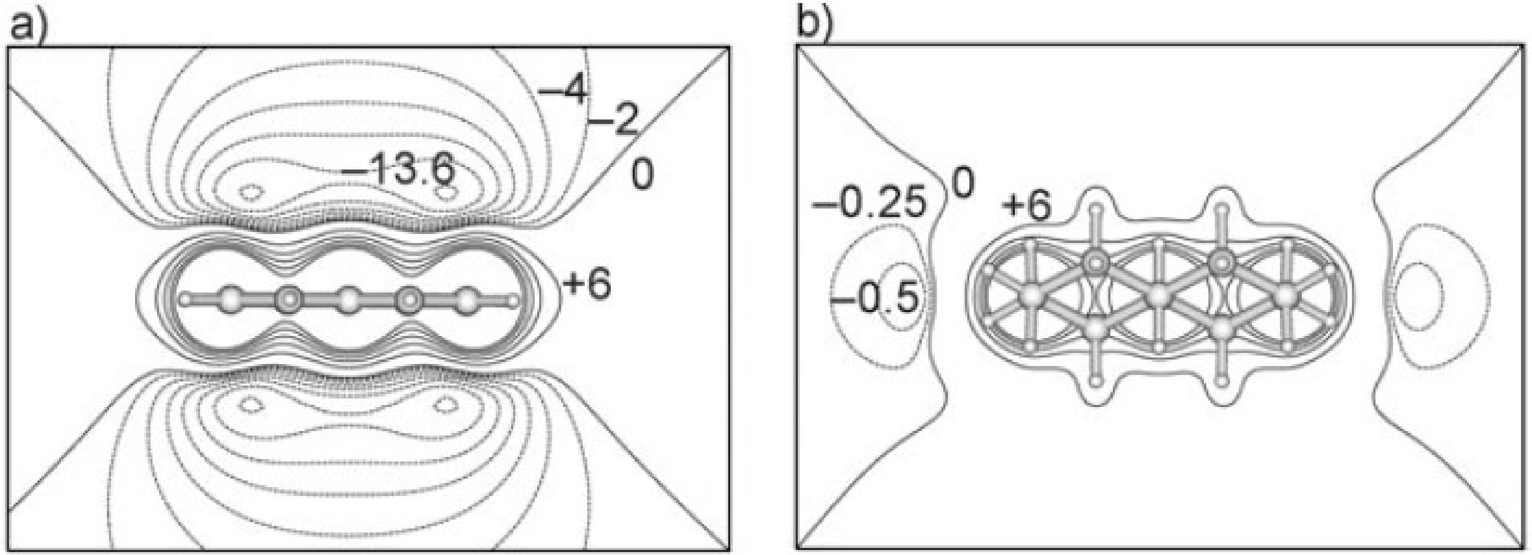


Figure 3. Electrostatic potentials (B97-D/TZV(2d,2p), isosurface values in kcal mol^{-1}) for a) naphthalene and b) decalin.

ES interaction disfavored

ES interaction favored

Energy decomposition analysis

- The first-order interaction

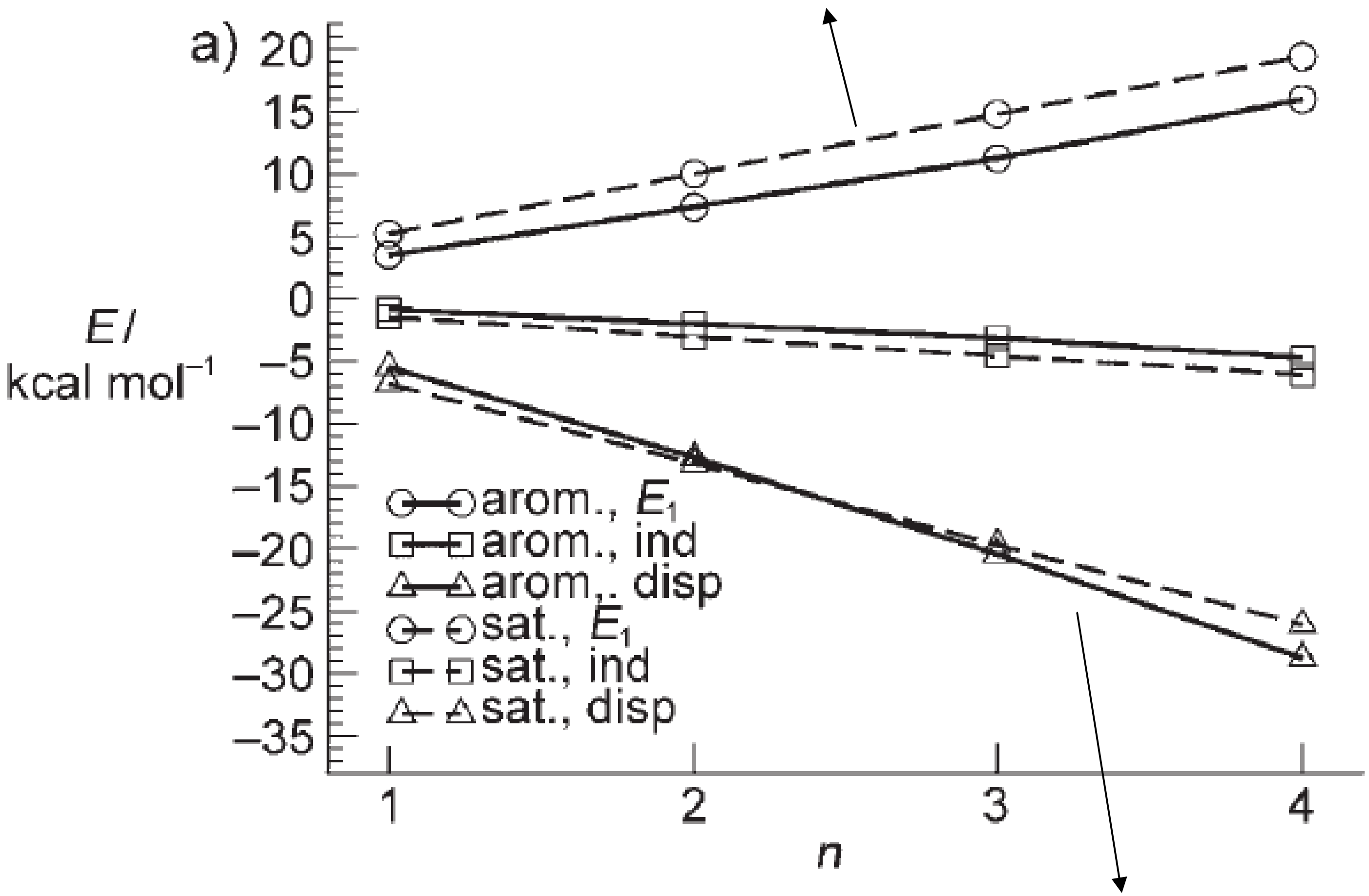
$$E_1 = E_{ES} + E_{EXR}$$

E_{EXR} = Pauli exchange repulsion

Table 2: Contributions[a] to the interaction energies (B2PLYP-D/TZV-(2d,p), [kcal mol^{-1}]) from an EDA.[b]

n	E_{EXR}	E_{ES}	E_1	E_{ind}	E^{disp}_{PT2}	E^{disp}_{DFT-D}
T-shaped, aromatic						
1	9.4	−7.8	1.6	−1.0	−1.8	−2.0
2	17.5	−14.1	3.4	−1.8	−3.7	−3.9
3	25.7	−20.4	5.3	−2.6	−5.9	−5.9
4	34.2	−26.9	7.3	−3.4	−8.1	−8.0
stacked, saturated						
1	19.9	−14.7	5.2	−1.5	−2.8	−4.1
2	37.5	−27.5	10.0	−3.0	−5.6	−7.6
3	55.1	−40.3	14.8	−4.6	−8.4	−11.3
4	72.2	−52.8	19.4	−6.1	−11.2	−14.9
stacked, aromatic						
1	12.0	−8.6	3.5	−0.8	−2.9	−2.6
2	27.6	−20.3	7.4	−2.0	−6.9	−5.8
3	44.2	−33.0	11.2	−3.1	−11.2	−9.2
4	62.6	−46.6	16.0	−4.7	−15.9	−12.9

E1 arom < E1 sat : Less repulsion for aromatic complex

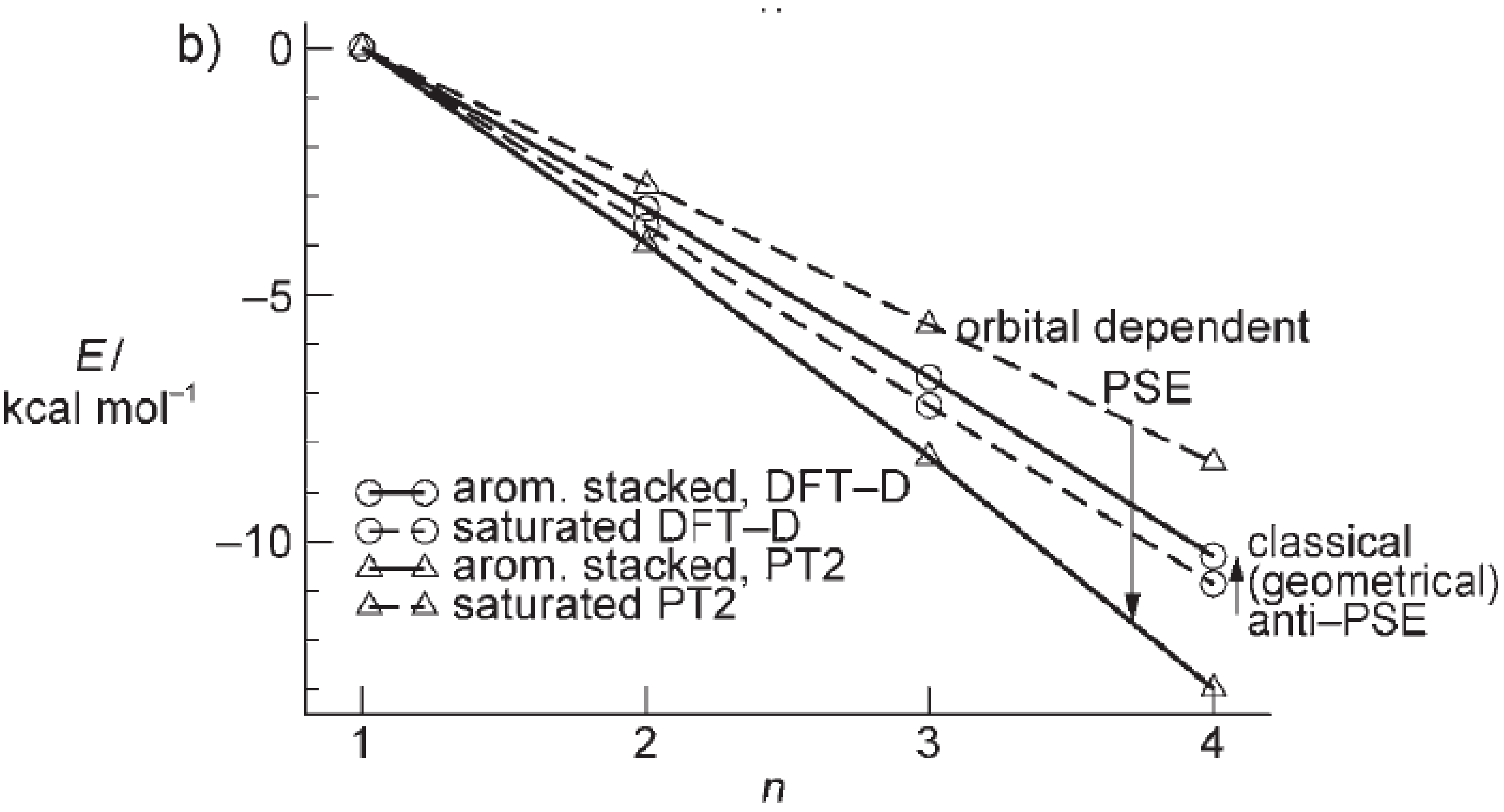


The increasing stability of the larger π -stacked dimers can be attributed almost exclusively to the dispersion component

- $E_{disp} = \bar{E}_{\mathrm{disp}}^{\mathrm{PT2}} + E_{\mathrm{disp}}^{\mathrm{DFT\text{-}D}}$

$\bar{E}_{\mathrm{disp}}^{\mathrm{PT2}}$: orbital-dependant

$E_{\mathrm{disp}}^{\mathrm{DFT\text{-}D}}$: a classical part



Orbital-dependant $E_{\text{disp}}^{\text{PT2}}$ is predominantly responsible for PSE.

E1

A special role of the π system

$E^{\mathrm{PT2}}_{\mathrm{disp}}$

Electron Correlation Contribution to the Interaction Energy

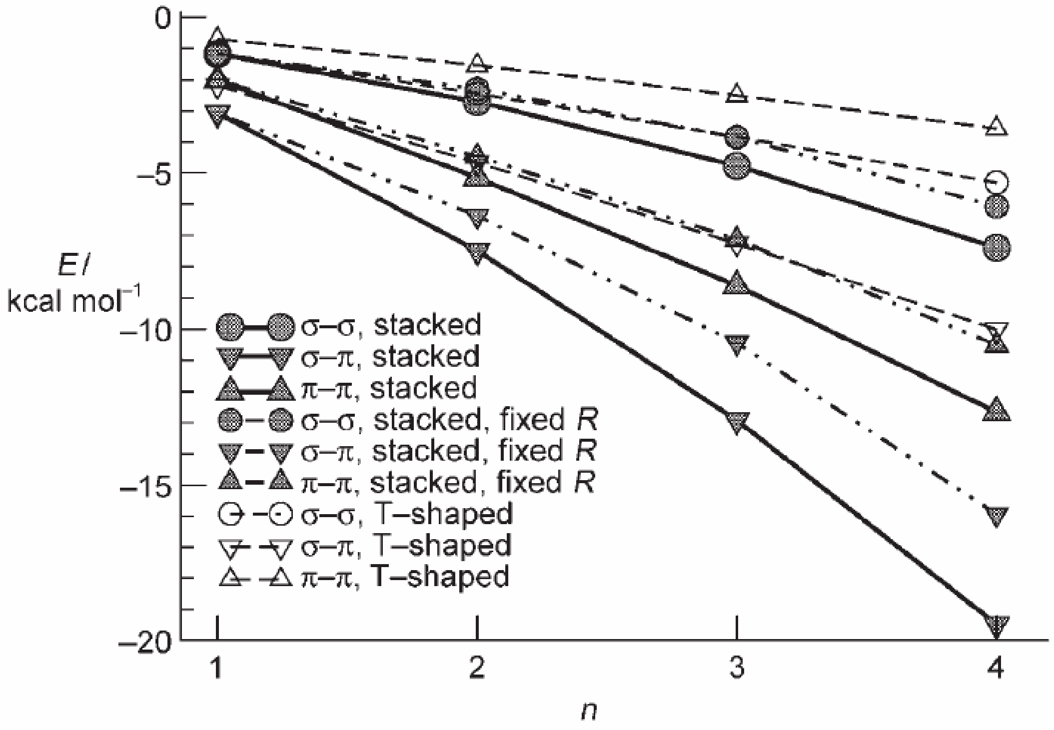


Figure 5. Correlation contributions to the interaction energies (counterpoise-uncorrected SCS-LMP2/TZV(2d,p)) for stacked arenes (——: fully energy-minimized complexes; –•–•: fixed interplane distance of 349 pm) and T-shaped complexes (-----).

- Both $\sigma-\pi$ and $\pi-\pi$ contributions distinguish the stacked aromatic orientation from the T-shaped orientation.

- Nonlinear curves rule out pure geometrical reasons.

Do Special Noncovalent π - π Stacking Interaction Really Exist?

- Yes
- Large unsaturated systems(>10 carbons)
- Spatially close----Stacked