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

\[ \pi - \pi \] 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 \( \pi - \pi \) stacking effect
• Polycyclic aromatic hydrocarbons (PAHs) vs. large alkanes
  PAHs become increasingly insoluble in common solvents with increasing size----
  **Compatible** with $\pi - \pi$ 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) \(\pi-\pi\) stacked. c), d) The cyclohexane dimer in two projections. The tetracene dimer: e) T-shaped and f) \(\pi-\pi\) 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 $\Delta E$

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<tr>
<th>Method</th>
<th>Number of Rings</th>
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<th>3</th>
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Table 1: Calculated interaction energies $-\Delta E$ [kcal mol$^{-1}$].

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

[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.$^{[33]}$
Intermolecular interaction energies $\Delta E$

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

*Figure 2.* Interaction energies $\Delta E$ [B2PLYP-D/QZV3P(1/2CP)] as a function of the number of rings $n$. 
• There is special interaction in the $\pi - \pi$ Stacked arrangement.

• Is the $\pi$ 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

\[ E_1 = E_{ES} + E_{EXR} \]

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

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<th>(E_{\text{EXR}})</th>
<th>(E_{\text{ES}})</th>
<th>(E_{1})</th>
<th>(E_{\text{ind}})</th>
<th>(E_{\text{disp}}^{\text{PT2}})</th>
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The increasing stability of the larger \( \pi \)-stacked dimers can be attributed almost exclusively to the dispersion component.

\[ E_1 \text{ arom} < E_1 \text{ sat} : \text{Less repulsion for aromatic complex} \]
$E_{\text{disp}} = E_{\text{disp}}^{\text{PT2}} + E_{\text{disp}}^{\text{DFT-D}}$

$E_{\text{disp}}^{\text{PT2}}$ : orbital-dependant

$E_{\text{disp}}^{\text{DFT-D}}$ : a classical part
Orbital-dependent $E_{\text{disp}}^{\text{PT2}}$ is predominantly responsible for PSE.
A special role of the $\pi$ system
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 $\pi - \pi$ Stacking Interaction Really Exist?

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