

Supporting Information for: “Reinterpreting π -Stacking”

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S1 Normalized Planarity Index (NPI)

Here we describe the NPI that was introduced in the context of Fig. 6. An MBD eigenvector ϕ consists of $3 \times N_{\text{atoms}}$ atomic displacement vectors $\vec{\phi}_i$ ($i = 1, \dots, N_{\text{atoms}}$), where each $\vec{\phi}_i$ is an atom-centered vector in three-dimensional space. Let \vec{u} and \vec{v} denote vectors that define the plane of interest, with

$$\vec{n} = \|\vec{u} \times \vec{v}\| \quad (\text{S1})$$

being a vector that is perpendicular to the \vec{u} - \vec{v} plane. The definition of this plane is arbitrary but the choice of a plane that bisects the center-to-center vector of the two monomers is convenient and intuitive. Mapping of the MBD eigenvectors onto the \vec{u} - \vec{v} plane is accomplished by subtracting the components of each eigenvector that lie orthogonal to the plane, to obtain new vectors

$$\vec{p}_i = \vec{\phi}_i - (\vec{n} \cdot \vec{\phi}_i) \vec{n} / \|\vec{n}\|^2. \quad (\text{S2})$$

The norm $\|\vec{p}_i\| \in [0, 1]$, with the value zero suggesting that the original eigenvector $\vec{\phi}_i$ is orthogonal to the reference plane and $\|\vec{p}_i\| = 1$ indicating that it is parallel to the reference plane. The total magnitude P for the the projected eigenvectors is a sum over the magnitudes of the projected eigenvectors that describe each oscillator,

$$P = \sum_i^{N_{\text{atoms}}} \left(\sum_{\alpha=x,y,z} p_{i\alpha}^2 \right)^{1/2}. \quad (\text{S3})$$

The NPI is taken to be the magnitude of the projected eigenvectors normalized to the number of atoms,

$$\text{NPI} = P / N_{\text{atoms}}. \quad (\text{S4})$$

S2 Additional Data

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| Molecule | ω/a_0^{-1} |
|---------------------------------|-------------------|
| benzene | 0.340 |
| naphthalene | 0.303 |
| anthracene | 0.288 |
| tetracene | 0.278 |
| pentacene | 0.268 |
| cyclohexane | 0.321 |
| perhydronaphthalene | 0.300 |
| perhydroanthracene | 0.287 |
| perhydrotetracene | 0.275 |
| perhydropentacene | 0.264 |
| C ₉₆ H ₂₄ | 0.230 |
| corannulene | 0.277 |

Table S1: Tuned range separation parameters computed using LRC- ω PBE/def2-TZVPPD.

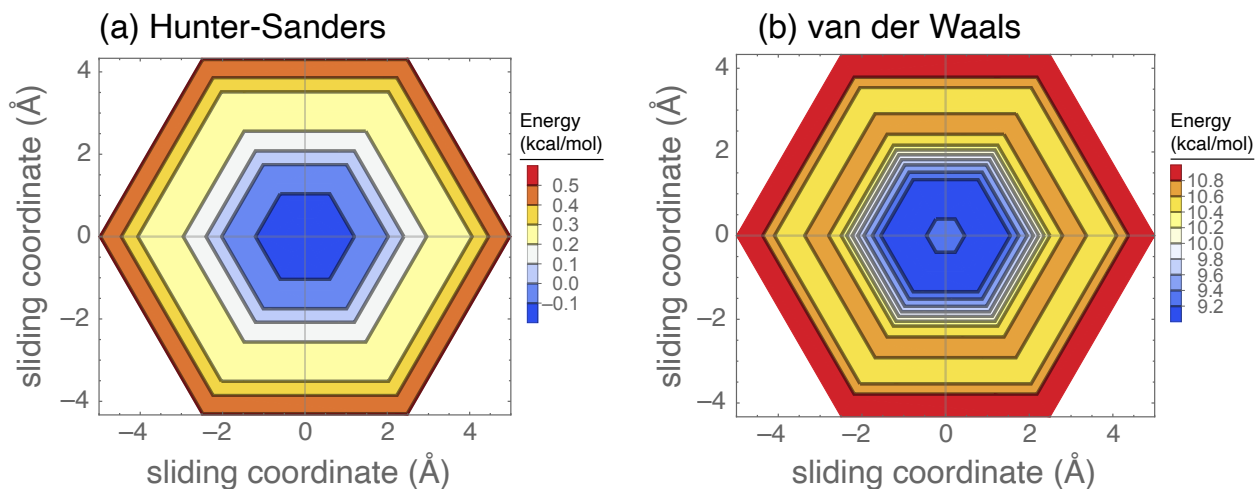
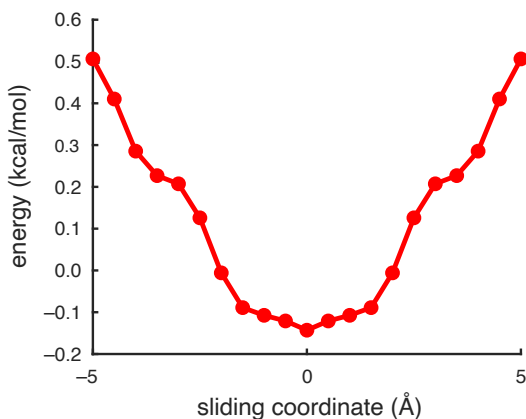


Figure S1: Two-dimensional potential surfaces for cofacial sliding of benzene along the surface of a C₉₆H₂₄ graphene nanoflake, using (a) the Hunter-Sanders electrostatic + dispersion model potential (Ref. 1) and (b) the vdW model potential from c The centers of the two molecules are aligned at the coordinate origin, which is a local minimum in (a) but a saddle point in (b). Note that the absolute energy scale for the vdW model is not meaningful, as the very simple parameterization in Ref. 2 does not include a short-range damping function.

(a) Hunter-Sanders



(b) van der Waals

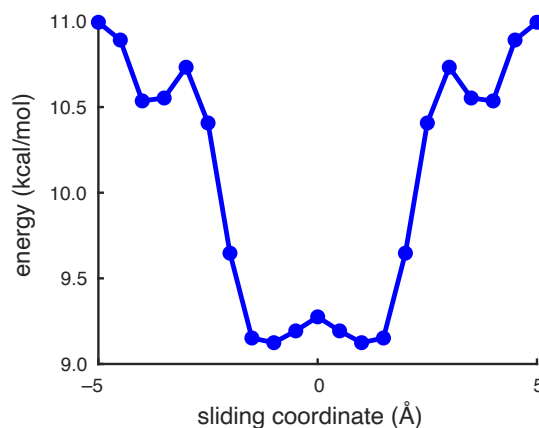


Figure S2: One-dimensional cross sections of the two-dimensional surfaces in Fig. S1, further elucidating the topography near the minimum. (a) The Hunter-Sanders model places benzene at the center of $C_{96}H_{24}$, whereas (b) the vdW model predicts that this is geometry is a saddle point, and instead predicts a slightly off-center structure as the minimum. Note that the absolute energy scale for the vdW model is not meaningful, as the very simple parameterization in Ref. 2 does not include a short-range damping function.

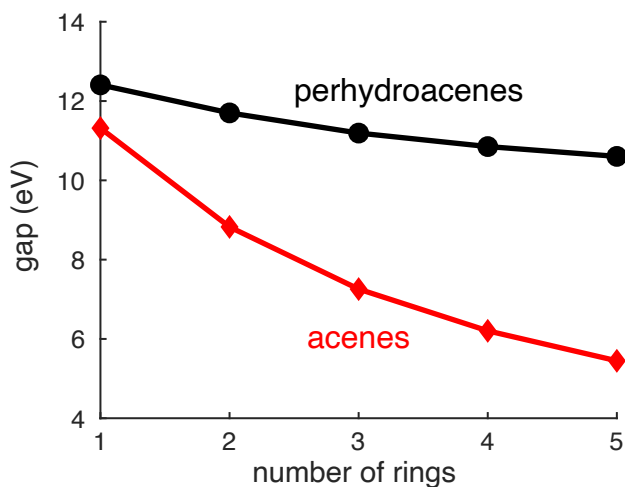


Figure S3: HOMO/LUMO gaps for linear acenes and their saturated analogues, computed at the LRC- ω PBE/def2-TZVPPD level.

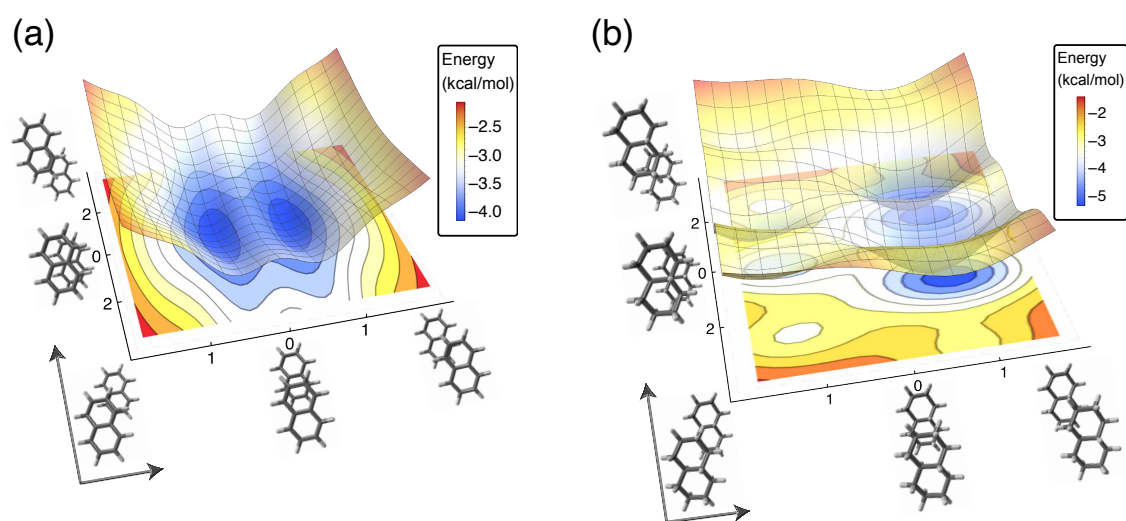


Figure S4: Two-dimensional scan of $E_{\text{elst+ind}}$ for (a) naphthalene dimer and (b) perhydronaphthalene dimer. The two-dimensional contours illustrate the topography of the potential surface and the cofacial sliding coordinates of the acene dimer and the analogues of the same displacements for perhydronaphthalene dimer.

References

- [1] Hunter, C. A.; Sanders, J. K. M. The nature of π - π interactions. *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.
- [2] Carter-Fenk, K.; Herbert, J. M. Electrostatics does not dictate the slip-stacked arrangement of aromatic π - π interactions. *Chem. Sci.* **2020**, *11*, 6758–6765.