

Supporting Information for:
Substituent and Heteroatom Effects on π - π Interactions: Evidence
That Parallel-Displaced π -Stacking Is Not Driven by Quadrupolar
Electrostatics

Brandon Schramm, Montgomery Gray, John M. Herbert*

*Department of Chemistry and Biochemistry
The Ohio State University, Columbus, Ohio 43210 USA*

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*herbert@chemistry.ohio-state.edu

S1 Computational Details

S1.1 XSAPT+MBD Method

To understand the XSAPT+MBD procedure it is helpful to start from the so-called ‘‘SAPT0’’ model for E_{int} ,¹⁻³ which is

$$E_{\text{int}}^{\text{SAPT0}} = \underbrace{E_{\text{elst}}^{(10)}}_{E_{\text{elst}}^{\text{SAPT0}}} + \underbrace{E_{\text{exch}}^{(10)}}_{E_{\text{exch}}^{\text{SAPT0}}} + \underbrace{E_{\text{disp}}^{(20)} + E_{\text{exch-disp}}^{(20)}}_{E_{\text{disp}}^{\text{SAPT0}}} + \underbrace{E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)}}_{E_{\text{ind}}^{\text{SAPT0}}} + \delta E_{\text{HF}} . \quad (\text{S1})$$

Superscripts (mn) in Eq. (S1) indicate that this model is zeroth-order in the Møller-Plesset fluctuation potentials, meaning that it uses Hartree-Fock wave functions for the monomers, while SAPT0 includes terms up to second order in the intermolecular Coulomb and exchange interactions. Second-order induction ($E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)}$) is usually augmented with an infinite-order correction, contained in the so-called $\delta(\text{Hartree-Fock})$ or δE_{HF} term. This is defined as

$$\delta E_{\text{HF}} = \Delta E_{\text{int}}^{\text{HF}} - \left(E_{\text{elst}}^{(10)} + E_{\text{exch}}^{(10)} + E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)} \right) , \quad (\text{S2})$$

where $\Delta E_{\text{int}}^{\text{HF}}$ is the Hartree-Fock interaction energy computed via the supramolecular approach.

In XSAPT+MBD, we identify

$$E_{\text{elst}}^{\text{XSAPT+MBD}} = E_{\text{elst}}^{(10)} \quad (\text{S3})$$

and

$$E_{\text{exch}}^{\text{XSAPT+MBD}} = E_{\text{exch}}^{(10)} , \quad (\text{S4})$$

which is the same as the SAPT0 model in Eq. (S1).

For the induction energy we have elsewhere experimented with omitting the $\Delta E_{\text{int}}^{\text{HF}}$ correction that is commonly used in SAPT0.⁴ However, it is included in all of the calculations reported here. Thus, we start from the SAPT0 induction energy,

$$E_{\text{ind}}^{\text{SAPT0}} = E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)} + \delta E_{\text{HF}} . \quad (\text{S5})$$

The present calculations also include point-charge embedding via the ‘‘XPol’’ procedure,^{5,6} by means of which atomic point charges are derived from the monomer self-consistent field (SCF) calculations and included in the SCF calculations for other monomers.^{6,7} In the present work, we employ CM5 embedding charges,⁸ whose accuracy for this purpose has been documented elsewhere.⁷ This procedure is implemented in the Q-Chem program.⁹

For a dimer system, the XSAPT induction energy thus includes a correction that amounts to the difference between the XSAPT total energy (with charge embedding) and the SAPT total energy (sans embedding),

$$\Delta E_{\text{XPol}} = E_{\text{XSAPT}} - E_{\text{SAPT}} . \quad (\text{S6})$$

(It is slightly unusual to consider SAPT *total* energies; see Ref. 10 for an explanation.) Putting this all together, the induction energy in XSAPT+MBD is

$$E_{\text{ind}}^{\text{XSAPT+MBD}} = E_{\text{ind}}^{\text{SAPT0}} + \Delta E_{\text{XPol}} . \quad (\text{S7})$$

The most important difference between SAPT0 and XSAPT+MBD is that the latter replaces the second-order dispersion in Eq. (S1) with the MBD model as defined in Ref. 7,

$$E_{\text{disp}}^{\text{XSAPT+MBD}} = E_{\text{MBD}} . \quad (\text{S8})$$

This is a slightly modified version¹¹ of the MBD model developed for DFT calculations by Tkatchenko and co-workers.¹² It achieves quantitative accuracy as compared to SAPT2+(3) calculations,^{3,4,11,13} whereas conventional second-order dispersion ($E_{\text{disp}}^{(20)} + E_{\text{exch-disp}}^{(20)}$) does not.¹⁴ Importantly, the individual energy components agree with SAPT2+(3) energy components,¹³ demonstrating that the accuracy of XSAPT+MBD is not an artifact of error cancellation and that the components can be taken seriously for interpretative purposes.

The energy components in Eqs. (S3), (S4), (S7), and (S8) constitute the elements of the energy decomposition in Eq. (3). The raw data needed to make the plots, in the form of these energy components for each system, are provided in a separate attachment.

S1.2 Electrostatics

S1.2.1 General

Qualitative descriptions of the various energy components in Eq. (3) can be found in a recent Perspective on electrostatic interactions.¹⁵ However, since electrostatics is a key aspect of the present work, we pause to explicate E_{elst} in more detail. The first-order SAPT electrostatic interaction ($E_{\text{elst}}^{(10)}$) is nothing other than the conventional Coulomb interaction between non-interacting monomer wave functions, computed at the SCF level.¹⁶ This means that E_{elst} in XSAPT+MBD can be partitioned into nuclear–nuclear ($E_{\text{elst}}^{\text{nn}}$), electron–electron ($E_{\text{elst}}^{\text{ee}}$), and electron–nuclear ($E_{\text{elst}}^{\text{en}}$) components,

$$E_{\text{elst}} = E_{\text{elst}}^{\text{nn}} + E_{\text{elst}}^{\text{ee}} + E_{\text{elst}}^{\text{en}} . \quad (\text{S9})$$

Although we do not separate these contributions in the present work, Eq. (S9) is introduced here in order to note that each separate contribution has a familiar form.

For a noncovalent complex $A \cdots B$ with isolated-monomer electron densities $\rho_0^{\text{A}}(\mathbf{r})$ and $\rho_0^{\text{B}}(\mathbf{r})$, computed in practice using Kohn-Sham DFT (Section S1.3), these three components are defined as¹⁵

$$E_{\text{elst}}^{\text{nn}} = \sum_{a \in A} \sum_{b \in B} \frac{Z_a Z_b}{R_{ab}} , \quad (\text{S10a})$$

$$E_{\text{elst}}^{\text{ee}} = \int \frac{\rho_0^{\text{A}}(\mathbf{r}_1) \rho_0^{\text{B}}(\mathbf{r}_2)}{\|\mathbf{r}_1 - \mathbf{r}_2\|} d\mathbf{r}_1 d\mathbf{r}_2 , \quad (\text{S10b})$$

and

$$E_{\text{elst}}^{\text{en}} = - \sum_{a \in A} \int \frac{Z_a \rho_0^{\text{B}}(\mathbf{r})}{\|\mathbf{r} - \mathbf{R}_a\|} d\mathbf{r} - \sum_{b \in B} \int \frac{Z_b \rho_0^{\text{A}}(\mathbf{r})}{\|\mathbf{r} - \mathbf{R}_b\|} d\mathbf{r} . \quad (\text{S10c})$$

Here, Z_a and Z_b are atomic numbers and these expressions are written in atomic units where $e^2/4\pi\epsilon_0 = 1$. The signs in Eq. (S10c) reflect the convention that electron densities are output from

electronic structure programs as strictly positive quantities, representing probability densities of negatively-charged electrons. To make contact with Eq. (2) in the main text, one should identify $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ in that equation as the *total* charge densities, including both nuclei and electrons, computed for the isolated monomers. (See, for example, the discussion in Ref. 15.)

S1.2.2 Multipolar

Multipolar electrostatics calculations in Section 3.4 were performed using standard formulas,¹⁷ which are briefly outlined here. The multipolar expansion of the electrostatic interaction between two charge-neutral molecules A and B is

$$\begin{aligned}
 U_{\text{elst}} = & - \sum_{\alpha,\beta} T_{\alpha\beta} \mu_{\alpha}^A \mu_{\beta}^B - \frac{1}{3} \sum_{\alpha,\beta,\gamma} T_{\alpha\beta\gamma} (\mu_{\alpha}^A \Theta_{\beta\gamma}^B - \Theta_{\alpha\beta}^A \mu_{\gamma}^B) \\
 & - \sum_{\alpha,\beta,\gamma,\delta} T_{\alpha\beta\gamma\delta} \left(\frac{1}{15} \mu_{\alpha}^A \Omega_{\beta\gamma\delta}^B - \frac{1}{9} \Theta_{\alpha\beta}^A \Theta_{\gamma\delta}^B + \frac{1}{15} \Omega_{\alpha\beta\gamma}^A \mu_{\delta}^B \right) + \dots
 \end{aligned}
 \tag{S11}$$

where $\alpha, \beta, \gamma, \delta \in \{x, y, z\}$ are Cartesian components of the various multipole tensors. These include the multipole interaction tensor $\mathbf{T}$, the dipole moment vector $\boldsymbol{\mu}$, and the quadrupole ($\boldsymbol{\Theta}$) and octupole ($\boldsymbol{\Omega}$) tensors. Quadrupole moment tensors in this expression are traceless: $\Theta_{\alpha\alpha} + \Theta_{\beta\beta} + \Theta_{\gamma\gamma} = 0$. Expressions for the elements of $\mathbf{T}$ can be found in Ref. 17.

For calculations reported in Section 3.4, we include up to 16-pole terms based on dipole and quadrupole moments computed at the optimally tuned LRC- ω PBE¹⁸/def2-TZVPD¹⁹ level of theory, which is consistent with the way that the monomers are described in the XSAPT+MBD calculations (see Section S1.3), thus consistent with the exact electrostatics calculations (E_{elst}). Traceless quadrupole moment tensors are computed directly from Q-Chem calculations, as described elsewhere,²⁰ in a coordinate system where the origin lies at the center of the arene ring (rather than at the center of mass or center of nuclear charge). Terms in Eq. (S11) involving the octupole moment tensor ($\boldsymbol{\Omega}$) are neglected, although for benzene the octupole moments are already zero by symmetry.

S1.3 SCF Procedure

The sum $E_{\text{elst}} + E_{\text{exch}} + E_{\text{ind}}$ in Eq. (3) looks much like SAPT0 but the relevant terms are evaluated using Kohn-Sham molecular orbitals, in what has sometimes been called ‘‘SAPT0(KS)’’.^{3,4} The use of Kohn-Sham orbitals represents a low-cost way to incorporate intramolecular electron correlation. Such calculations must employ functionals that are asymptotically correct,^{4,21–23} else they are subject to artifacts arising from too-small HOMO/LUMO gaps. Correct asymptotic behavior is readily achieved using monomer-specific tuning^{4,14,23} of the range-separation parameter ω in a long-range corrected (LRC) density functional.^{18,24,25} (The LRC- ω PBE functional¹⁸ is used for the present calculations.) The tuning procedure, which is described elsewhere,⁴ is based upon the global density-dependent (‘‘ ω_{GDD} ’’) scheme developed by Modrzejewski *et al.*²⁶ It is a computationally facile approximation to ‘‘optimal tuning’’ or ‘‘IE tuning’’ based on the ionization energy (IE) theorem of DFT.²⁷ The ω_{GDD} procedure also avoids some problems associated with IE-tuning for large conjugated molecules.⁴

All calculations reported here employ ω_{GDD} -tuned LRC- ω PBE calculations for the monomers. In addition, the SCF calculations use the “XPol” procedure,^{5,6} with CM5 embedding charges^{7,8} that are derived from the monomer wave functions, is used to polarize the monomer SCF densities. This offers a slightly improvement in accuracy for dispersion-bound complexes,⁴ because the polarized density is used to compute the MBD dispersion energy, though the effect is small.

All calculations were performed using Q-Chem.⁹ For the SCF calculations, the integral drop screening threshold and the shell-pair drop tolerance were both set to 10^{-14} a.u.. (This is typically done to avoid problems with linear dependencies²⁸ but those are unlikely to be a problem for the small systems considered here.) The SCF convergence threshold was set to 10^{-5} a.u.. We used the def2-TZVPD basis set²⁹ for the XSAPT+MBD calculations, as this affords converged results for each energy component.¹³ For the δE_{HF} correction, the 6-311G basis set was used instead, as this term contributes only to the (already small) induction energy, and furthermore our testing confirms that this correction is rather insensitive to basis set.¹³

S1.4 Geometries

Monomer geometries for the nitrogen-containing heterocycles were optimized at the ω B97X-V/def2-TZVPD level.^{29,30} The other monomer geometries were taken from the work of Wheeler and Houk,³¹ who previously considered substituent effects on stacking energies. These monomer geometries are provided in a separate attachment.

To obtain optimal face-to-face separations (R), we wanted to keep the aromatic ring structures strictly coplanar. This is challenging to do in a geometry optimization (and in any case, XSAPT+MBD gradients are not available), so the following three-step procedure was used instead. First, the minimum-energy separation for the cofacial arrangement was determined via a one-dimensional scan from 2.5 Å to 4.3 Å in increments of 0.2 Å. From that optimal cofacial geometry, a second potential energy scan was performed in which one monomer was translated along a parallel-sliding coordinate until the ring centers were 3 Å apart when projected onto the parallel plane between the two aromatic moieties. This parallel-displaced minimum-energy structure was then used for a second scan along the face-to-face separation coordinate, from $R = 2.5$ Å to $R = 4.4$ Å in increments of 0.1 Å. The minimum-energy separation in the parallel-displaced configuration, obtained in this way, is the value of R that is used in Figs. 4, 5, and 9. Monomer geometries were kept rigid throughout this process.

Optimal values of R for both the sandwich and parallel-displaced arrangements of several homomolecular dimers, determined by the procedure outlined above, are listed in Table S1. For the benzonitrile dimer, we repeated this procedure at the ω B97X-V/def2-TZVPD level as a check. In that case, the same optimal separations are obtained for both the sandwich configuration ($R_{\text{sandw}} = 3.9$ Å) and the parallel-displaced arrangement ($R_{\text{PD}} = 3.55$ Å), to within the width of the increments used in the coordinate scans.

Data for the two-dimensional surfaces were then generated via translations along different radial axes as shown in Fig. S1, fixing one monomer in space.

S2 References

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S3 Additional Figures & Tables

Table S1: Face-to-face separations (R) for various homomolecular dimers, determined using XSAPT+MBD via the procedure outlined in Section S1.4.

Monomer	R (Å)	
	sandwich	parallel-displaced
benzene	3.4	3.8
benzonitrile	4.1	3.5
phenol	3.9	3.4
pyridine	3.9	3.5
thiophene	4.0	3.6
toluene	3.9	3.5
triazine	3.7	3.5

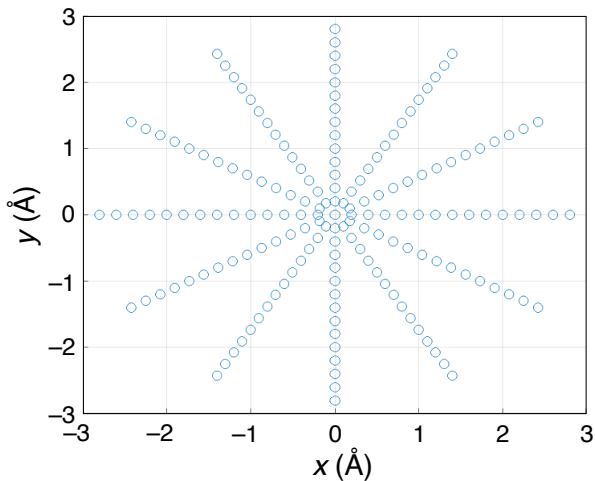


Fig. S1: Radial translations used to generate two-dimensional potential energy surfaces at a given value of the face-to-face separation, R .

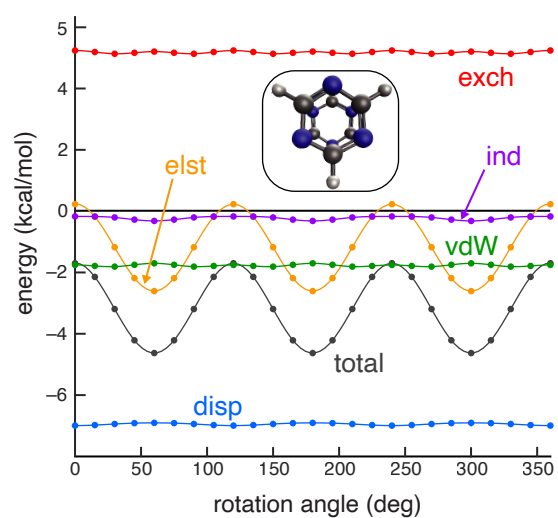


Fig. S2: Energy profile of (1,3,5-triazine)₂ at $R = 3.4$ Å, as one monomer is rotated around its central C_3 axis while the other is held fixed.