SUPPORTING INFORMATION

How different are Electron-rich and Electron-deficient π Interactions?

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Contents

- 1. Details of Symmetry-Adapted Perturbation Theory Calculations
- 2. Criteria used for Cambridge Structural Database search and results
- 3. Quadrupole moments and NBO charges of monomers.
- 4. Calculated structural isomers and energies of π -dimer complexes
- 5. Complete list of authors for citations with 16 or more authors

1. Details of Symmetry-Adapted Perturbation Theory Calculations

The total interaction energy was decomposed into electrostatic (es), induction (ind), dispersion (disp) and exchange-repulsion (exch) components based on Symmetry-Adapted Perturbation Theory (SAPT), written as

$$\begin{split} E_{tot} &= E_{es} + E_{exch} + E_{ind} + E_{disp} + \delta_{ind,resp}^{HF} \\ &= E_{es} + E_{exch}^* + E_{ind*} + E_{disp*} + \delta_{ind,resp}^{HF} \end{split}$$

where

$$\begin{split} E_{es} &= E_{es}^{(10)} + E_{es,resp}^{(12)} \\ E_{ind} &= E_{ind,resp}^{(20)} \\ E_{disp} &= E_{disp}^{(20)} \\ E_{exch} &= E_{exch}^{(10)} + E_{exch}^{(11)} + E_{exch}^{(12)} + E_{exch,ind,resp}^{(20)} + E_{exch,disp}^{(20)} \end{split}$$

The superscripts refer to orders in the intermolecular interactions and intramolecular correlation potential, respectively, "resp" to the inclusion of coupled Hartree-Fock response and $\delta_{ind,resp}^{HF}$ to higher order Hartree-Fock induction and exchange-induction contributions. In the present study, the definitions are modified as follows

$$\begin{split} E_{in} &\equiv E_{ind*} = E_{ind,resp}^{(20)} + E_{exchind,resp}^{(20)} + \delta_{ind,resp}^{(HF)} + E_{ind}^{(22)} + E_{ex,ind}^{(22)} \\ E_{dp} &\equiv E_{disp**} = E_{disp}^{(20)} + E_{exch,disp}^{(20)} + \left(E_{CCSD(T)/CBS} - E_{SAPT(MP2)/aVDZ'}\right) \\ E_{x} &\equiv E_{exch*} = E_{exch}^{(10)} + E_{exch}^{(11)} + E_{exch}^{(12)} \end{split}$$

which is a more appropriate classification of similar types of π -interaction. The CCSD(T)/CBS total energy was added to correct the basis set dependency of the dispersion energy.

2. Criteria used for Cambridge Structural Database search and Results

The Cambridge Structural Database (CSD) version 5.31 (November 2009) was used to search for organic crystals containing benzene, pyridine, pyrazine, triazine and tetrazine fragments. Only unsubstituted rings were considered. Definitions in the geometry of the two arene fragments are illustrated in Figure 1 in the main text. Constraints were imposed on the centroid-centroid distance R_c (3–6 Å) and interplanar angle (0–90°). The centroid-centroid-edge atom angle α was defined to account for ring tilt and was set to 90±30°. The horizontal displacement R_d was calculated from R_c and the vertical separation R_v . Analysis was restricted to fragments with $R_d < 2$ Å and $R_v < 5$ Å. 42, 67, 5, 4 and 3 fragments were found for benzene, pyridine, pyrazine, triazine and tetrazine, respectively.



Figure S1: Plot of (a) distance between the nearest C or N atom in one monomer to the center of the other (R_v) and (b) torsion angle spanning the 2 ring centers and 2 N atoms against the interplanar angle for pyridine (Py) and pyrazine (Pz).

3. Quadrupole moments and NBO charges of monomers.

Table S1: Quadrupole moments (D Å) at the HF/6-311G** level and NBO charges at the MP2/aug-cc-pVDZ level.

	Q	С	N	Н
Benzene	-8.76	-0.219		0.219
Pyridine	-5.60	0.103/-0.293/-0.152	-0.547	0.203/0.226/0.223
Pyrazine	-2.43	0.030	-0.482	0.211
Triazine	0.99	0.447	-0.645	0.197
Tetrazine	3.32	0.266	-0.240	0.214



4. Calculated Structural Isomers and Energies of π -dimer complexes

Figure S2: Optimized geometries of N-containing heterocyclic dimers with parallel (first two rows) and T-shaped structures (last two rows) at the RI-MP2/aug-cc-pVDZ level with BSSE-correction. In the main text, the lowest energy structure between D^L (antiparallel orientations between two monomers) and D^r (perpendicularly rotated orientations between two monomers) is simply represented as structure D.

Table S2: Total interaction energy and components of important conformers at the SAPT(MP2)/aug-cc-pVDZ' level calculated using RI-MP2/aug-cc-pVDZ optimized geometries. Values are corrected for CCSD(T) energy and given in kcal/mol.

T-shaped dimers										
	$Bz-T^{H}$	Py-T ^H	Py-T ^N	Pz-T ^H	Pz-T ^N	Tr-T ^H	Tr-T ^N	Tt-T ^H	Tt-T ^N	
E _{es}	-2.15	-3.23	-2.62	-2.20	-4.76	-1.51	-4.44	0.60	-6.19	
$E_{ind^{\ast}}$	-0.64	-0.78	-1.01	-0.65	-0.93	-0.63	-0.68	-0.42	-1.11	
E _{disp**}	-4.63	-4.83	-4.84	-4.42	-5.23	-3.94	-4.77	-3.03	-4.66	
E _{exch*}	4.57	5.29	5.89	4.56	7.57	3.87	6.45	1.93	7.69	
E _{tot}	-2.84	-3.56	-2.57	-2.70	-3.36	-2.22	-3.44	-0.91	-4.27	

Parallel dimers										
	Bz-D	$Py-D^L$	Pz-D ^r	Tr-D ^L	Tt-D ^r	Bz-S	Py-S	Pz-S	Tt-S	Tt-S
Ees	-2.92	-4.48	-4.94	-3.00	-3.46	-0.71	-2.21	-3.42	-2.75	-2.31
$E_{ind^{\ast}}$	-0.96	-0.99	-1.06	-0.52	-1.19	-0.32	-0.37	-0.31	-0.40	-0.44
E _{disp**}	-7.89	-8.11	-8.48	-7.39	-8.25	-5.96	-6.38	-6.93	-6.94	-7.14
E _{exch*}	9.14	9.78	10.39	7.09	9.23	5.46	6.17	7.18	6.18	6.76
E _{tot}	-2.62	-3.80	-4.09	-3.82	-3.67	-1.53	-2.79	-3.48	-3.92	-3.13

Dimer	Geometrical Parameters						Interaction Energy (kcal/mol)					
-	R _c	R _v	R _d	Θ	φ	-	MP2			D(T)		
		•	u		· · ·	aVDZ	aVTZ	CBS	aVDZ	CBS		
Bz-S	3.75	3.75	0.00			-2.91	-3.22	-3.38	-1.10	-1.53		
Bz-D	3.74	3.41	1.55			-4.29	-4.71	-4.93	-2.06	-2.62		
$Bz-T^H$	4.93	4.87	0.71			-3.32	-3.59	-3.72	-2.46	-2.84		
Py-S	3.62	3.62	0.00	0.0		-4.17	-4.50	-4.64	-2.32	-2.79		
$Py-D^L$	3.61	3.56	0.65	6.1		-5.59	-6.01	-6.19	-3.21	-3.80		
Py-D ^r	3.63	3.34	1.41	0.0		-5.24	-5.72	-5.92	-2.80	-3.48		
Py-D1	3.61	3.37	1.30	0.0		-5.41	-5.82	-5.99	-2.92	-3.50		
Py-D2	3.63	3.37	1.36	0.1		-4.19	-4.61	-4.79	-2.20	-2.80		
Py-T ^H	4.86	4.62	1.51		0.0	-4.08	-4.35	-4.46	-3.19	-3.56		
Py-T ^N	4.59	4.47	1.08		0.0	-3.08	-3.40	-3.53	-2.12	-2.57		
Py-T1	4.88	4.62	1.59		0.0	-3.94	-4.20	-4.31	-3.08	-3.45		
2												
Pz-S	3.48	3.48	0.00	0.0		-5.24	-5.59	-5.74	-2.98	-3.48		
$Pz-D^L$	3.66	3.29	1.62	0.0		-3.95	-4.34	-4.50	-1.85	-2.40		
Pz-D ^r	3.48	3.21	1.35	2.3		-6.10	-6.56	-6.76	-3.43	-4.09		
Pz-D1	3.62	3.62	0.00	0.1		-4.49	-4.84	-4.99	-2.27	-2.77		
$Pz-T^H$	4.81	4.59	1.44		0.0	-3.17	-3.40	-3.50	-2.38	-2.70		
Pz-T ^N	4.40	4.36	0.56		0.0	-4.18	-4.51	-4.65	-2.89	-3.36		
Pz-T1	4.36	4.36	0.00		0.0	-4.13	-4.45	-4.59	-2.79	-3.25		
Pz-T2	4.83	4.83	0.01		0.0	-2.78	-2.96	-3.03	-2.09	-2.34		
Tr-S	3.43	3.43	0.00	0.0		-4.53	-4.86	-5.00	-3.45	-3.92		
$Tr-D^{L}$	3.43	3.34	0.80	-0.1		-4.69	-5.06	-5.22	-3.29	-3.82		
Tr-D ^r	3.51	3.31	1.17	0.0		-4.06	-4.50	-4.69	-2.48	-3.12		
Tr-D1	3.43	3.31	0.91	0.0		-4.67	-5.00	-5.13	-3.20	-3.67		
Tr-D2	3.67	3.55	0.90	1.4		-3.84	-4.19	-4.34	-2.51	-3.01		
Tr-T ^H	4.73	4.44	1.63		0.0	-2.33	-2.56	-2.65	-1.89	-2.22		
Tr-T ^N	4.40	4.36	0.62		-3.6	-3.76	-4.05	-4.18	-3.02	-3.44		
Tr-T1	4.36	4.36	0.06		90.1	-3.63	-3.92	-4.04	-2.83	-3.25		
Tt-S	3.33	3.33	0.01	0.0		-5.22	-5.52	-5.64	-2.71	-3.13		
$Tt-D^L$	3.51	3.32	1.15	0.0		-2.42	-2.76	-2.91	-0.56	-1.04		
Tt-D ^r	3.35	3.25	0.83	-0.2		-5.86	-6.29	-6.47	-3.06	-3.67		
Tt-D1	3.72	3.70	0.38	0.0		-4.90	-5.29	-5.45	-2.71	-3.26		
Tt-T ^H	4.91	4.91	0.00		0.0	-1.17	-1.33	-1.40	-0.69	-0.91		
Tt-T ^N	4.29	4.29	0.05		90.1	-5.18	-5.54	-5.70	-3.75	-4.27		
Tt-T1	4.28	4.21	0.79		0.0	-4.83	-5.22	-5.39	-3.44	-3.99		
Tt-T2	4.39	4.39	0.06		0.0	-4.02	-4.44	-4.61	-2.89	-3.48		
Tt-T3	4.41	4.41	0.06		90.0	-3.40	-3.81	-3.98	-2.39	-2.97		
Tt-T4	5.11	5.11	0.00		90.0	-0.24	-0.34	-0.38	0.04	-0.09		

Table S3: Geometric and energetic characterization of N-containing heterocyclic dimers. Optimization was performed at the RI-MP2/aug-cc-pVDZ level. R_c , R_v and R_d are given in Å; θ and ϕ angles in degrees (definitions in Figure 1). Values are BSSE-corrected.

In the main text, the lowest energy structure between D^L (antiparallel orientations between two monomers) and D^r (perpendicularly rotated orientations between two monomers) is simply represented as structure D.

Dimer		Geometr	rical Param	Interacti	on Energy	(kcal/mol)			
	R _c	R_v	R _d	θ	φ	MP	2	CCS	D(T)
						aVTZ	aVQZ	CBS aVTZ	CBS
$Py-D^L$	3.55[3.61]	3.49[3.55]	0.63[0.66]	6.1[6.2]		-6.03 [-4.98]	-6.15 -	-6.20	
Py-T ^H	4.77	4.57	1.36		0.0	-4.35	-4.47 -	4.52	
Pz-D ^r	3.42[3.48]	3.15[3.22]	1.33[1.33]	2.3[1.9]		-6.59 [-5.42]	-6.79 -	-6.88	
Pz-T ^N	4.33	4.30	0.48		0.0	-4.52	-4.66 -	4.72	
Tr-S	3.37[3.44]	3.37[3.44]	0.00	0.0		-4.88 [-3.96]	-5.06 -	-5.13	
Tr-D ^L	3.38	3.27	0.85	-0.1		-5.08	-5.26 -	-5.34 -3.48	-3.73
Tr-T ^N	4.34	4.30	0.63		-0.8	-4.07	-4.20 -	4.25	
Tt-D ^r	3.30	3.18	0.86	0.3		-6.32	-6.53 -	-6.62	
Tt-T ^N	4.41[4.30]	4.41[4.30]	0.07[0.04]		90.2[90.1]	-5.56 [-4.77]	-5.73 -	5.80 -4.01	-4.25

Table S4: Geometric and energetic characterization of N-containing heterocyclic dimers. Optimization was performed at the RI-MP2/aug-cc-pVTZ [RI-MP2/cc-pVTZ] level. R_c , R_v and R_d are given in Å; θ and ϕ angles in degrees (definitions in Figure 1). Values are BSSE-corrected.

1. Results from the counterpoise-corrected optimization at RI-MP2/cc-pVTZ level for the most stable dimers (Py-D^L, Pz-D^r, Tr-S and Tt-T^N) are similar to that of RI-MP2/aug-cc-pVDZ optimization. R_c and R_v have average absolute error of 0.01 Å and 0.01 Å. R_d and angle parameters are nearly identical in both the methods.

2. Results from the counterpoise-corrected optimization at RI-MP2/aug-cc-pVTZ level for the most stable displaced-stacked and T-shaped dimers are compared with that of RI-MP2/aug-cc-pVDZ results. R_c and R_v have average absolute error of 0.07 Å and 0.08 Å. R_d and angle parameters are nearly identical in both the methods.

3. RI-MP2/CBS (most stable dimers) and CCSD(T)/CBS energies (Tr-D^L and Tt-T^N) derived from aVTZ-aVQZ extrapolation have the average absolute error of 0.09 kcal/mol and 0.04 kcal/mol in comparison to that the RI-MP2/CBS and CCSD(T)/CBS energy values calculated from aVDZ-aVTZ extrapolation.



Figure S3: Correlation plot between respective energy components and interaction energy of S and D-series (left) along with T^{H} and T^{N} -series (right). R^{2} values for the electrostatic, induction, exchange-repulsion and dispersion contributions are shown.

5. Complete list of authors for citations with 16 or more authors

- (18) SAPT2008: An *Ab Initio* Program for Many-Body Symmetry-Adapted Perturbation Theory Calculations of Intermolecular Interaction Energies by R. Bukowski, W. Cencek, P. Jankowski, M. Jeziorska, B. Jeziorski, S. A. Kucharski, V. F. Lotrich, A. J. Misquitta, R. Moszýnski, K. Patkowski, R. Podeszwa, S. Rybak, K. Szalewicz, H. L. Williams, R. J. Wheatley, P. E. S. Wormer and P. S. Zuchowski, see also: ref. 1.
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