Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Electrostatic Penetration Effects Stand at the Heart of Aromatic π Interactions

Enrique M. Cabaleiro-Lago[a] , Jesús Rodríguez-Otero[b], Saulo A. Vázquez[b]

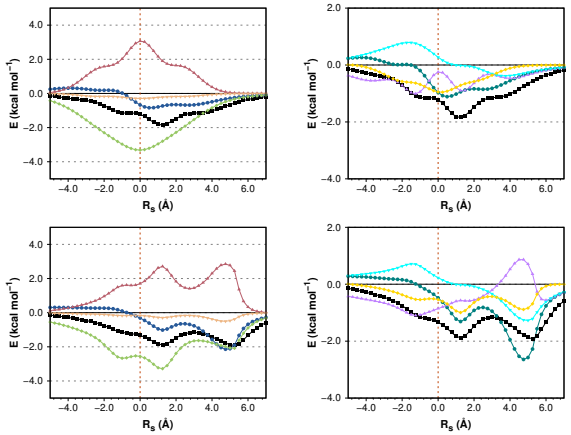
[a.] *Facultade de Ciencias (Dpto. de Química Física), Universidade de Santiago de Compostela, Campus de Lugo. Avda. Alfonso X El Sabio s/n 27002 Lugo, Galicia (Spain).*
[b.] *Facultade de Química (Dpto. de Química Física), Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Galicia (Spain).*

Table S1. Interaction energies and their components (kcal mol^{-1}) as obtained for the optimal distances (R_v and R_s, see Figure 1). Positive and negative R_s values as defined in Figure 1.

		$R_{v,min}$	$R_{s,min}$	E_{tot}	E_{ele}	E_{rep}	E_{ind}	E_{dis}	$E_{ele+ind}$	$E_{rep+dis}$	E_{pen}	E_{DMA}	%pen
C_6H_6	P	3.44	-1.79	-2.88	-2.02	6.89	-0.75	-7.00	-2.77	-0.11	-3.23	1.21	33
$C_6H_3F_3$	P	3.51	-1.14	-3.96	-3.04	7.01	-0.56	-7.36	-3.61	-0.35	-2.63	-0.42	24
$C_3H_3N_3$	P	3.37	-1.34	-3.89	-3.21	7.07	-0.77	-6.97	-3.98	0.10	-2.91	-0.30	27
$N_3H_6B_3$	P	3.69	-1.07	-2.13	-0.86	3.85	-0.29	-4.83	-1.15	-0.98	-1.49	0.64	25
C_6F_6	P	3.39	-0.99	-6.52	-6.19	9.65	-1.07	-8.91	-7.26	0.74	-3.54	-2.65	22
C_6H_{12}	P	4.24	-0.18	-2.73	-1.71	4.07	-0.51	-4.57	-2.22	-0.50	-1.55	-0.16	23
C_6H_6	P	3.44	1.79	-2.88	-2.02	6.89	-0.75	-7.00	-2.77	-0.11	-3.23	-0.69	18
$C_6H_3F_3$	P	3.37	1.50	-4.61	-4.21	8.65	-0.81	-8.25	-5.02	0.41	-4.16	0.30	23
$C_3H_3N_3$	P	3.47	1.23	-3.59	-2.71	5.98	-0.52	-6.33	-3.23	-0.35	-2.26	0.23	18
$N_3H_6B_3$	P	3.41	1.64	-2.98	-2.37	6.26	-0.62	-6.26	-2.98	0.00	-3.26	-0.28	17
C_6F_6	P	3.39	0.99	-6.52	-6.19	9.65	-1.07	-8.91	-7.26	0.74	-3.54	0.88	27
C_6H_{12}	P	3.98	1.47	-2.99	-1.91	4.79	-0.52	-5.35	-2.43	-0.56	-1.80	-0.12	23
C_6H_6	T	4.84	-1.21	-2.70	-1.78	3.48	-0.48	-3.93	-2.25	-0.45	-1.09	-0.65	19
$C_6H_3F_3$	T	4.90	-1.16	-1.86	-0.76	2.70	-0.28	-3.51	-1.05	-0.81	-1.07	0.20	23
$C_3H_3N_3$	T	5.08	0.00	-1.34	-0.31	1.70	-0.17	-2.55	-0.48	-0.86	-0.54	0.40	21
$N_3H_6B_3$	T	4.93	-1.15	-1.74	-0.97	2.27	-0.23	-2.82	-1.20	-0.54	-0.69	-0.22	17
C_6F_6	T	4.85	-1.19	-1.71	-0.34	2.70	-0.40	-3.68	-0.74	-0.97	-1.21	1.00	29
C_6H_6	T	4.84	1.21	-2.70	-1.78	3.48	-0.48	-3.93	-2.25	-0.45	-1.09	1.21	33
$C_6H_3F_3$	T	4.83	1.22	-2.23	-1.13	3.00	-0.29	-3.80	-1.42	-0.80	-1.06	-0.05	31
$C_3H_3N_3$	T	4.79	1.25	-1.88	-1.02	2.72	-0.29	-3.28	-1.31	-0.57	-1.00	-0.02	22
$N_3H_6B_3$	T	4.93	1.05	-1.77	-0.83	2.22	-0.25	-2.92	-1.07	-0.70	-0.60	0.90	35
C_6F_6	T	4.85	1.19	-1.71	-0.34	2.70	-0.40	-3.68	-0.74	-0.97	-1.21	-2.65	22
C_6H_6	T2	4.81	-1.24	-2.75	-1.83	3.59	-0.48	-4.03	-2.32	-0.44	-1.19	-0.69	18
$C_6H_3F_3$	T2	4.84	-1.22	-2.07	-0.95	2.92	-0.29	-3.75	-1.24	-0.83	-1.14	-0.07	20
$C_3H_3N_3$	T2	4.88	-1.09	-1.48	-0.36	2.07	-0.21	-2.98	-0.57	-0.91	-0.76	-1.22	16
$N_3H_6B_3$	T2	4.91	-1.16	-1.78	-0.92	2.30	-0.23	-2.92	-1.15	-0.63	-0.70	-0.23	15
C_6F_6	T2	4.83	-1.21	-1.72	-0.30	2.75	-0.40	-3.76	-0.70	-1.02	-1.29	0.88	27
C_6H_6	T2	4.81	1.24	-2.75	-1.83	3.59	-0.48	-4.03	-2.32	-0.44	-1.19	-0.65	19
$C_6H_3F_3$	T2	4.84	1.22	-2.07	-0.95	2.92	-0.29	-3.75	-1.24	-0.83	-1.14	0.20	23
$C_3H_3N_3$	T2	4.88	1.09	-1.48	-0.36	2.07	-0.21	-2.98	-0.57	-0.91	-0.76	0.40	21
$N_3H_6B_3$	T2	4.91	1.16	-1.78	-0.92	2.30	-0.23	-2.92	-1.15	-0.63	-0.70	-0.22	17
C_6F_6	T2	4.83	1.21	-1.72	-0.30	2.75	-0.40	-3.76	-0.70	-1.02	-1.29	1.00	29

Second minimum **C_6H_6-$C_3H_3N_3$ T:**

$C_3H_3N_3$	T	2.61	5.24	-1.92	-1.92	2.48	-0.39	-2.10	-2.31	0.39	-0.70	-0.46	24



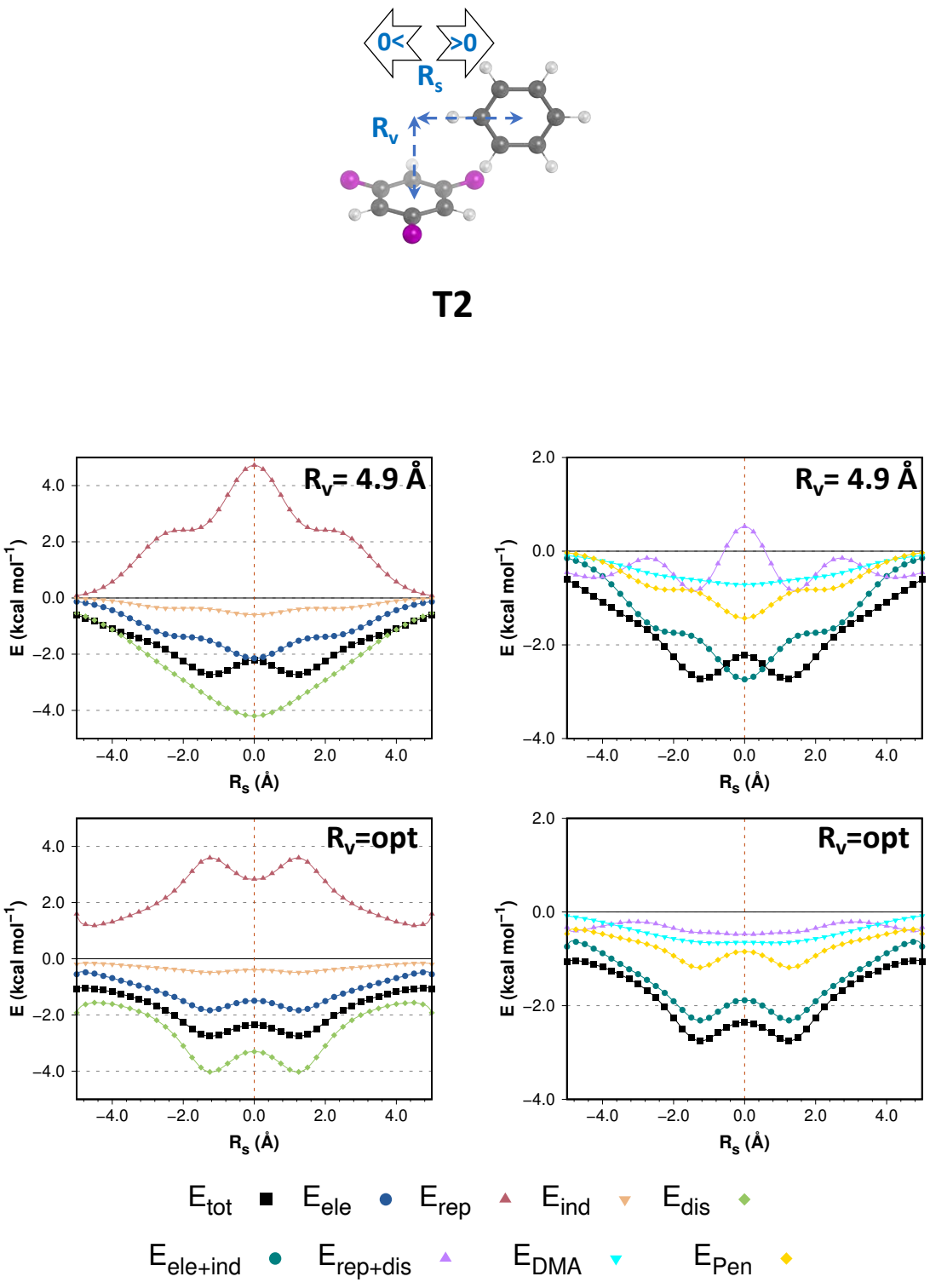


Figure S1. Potential energy curves for benzene dimer as obtained with SAPT0/jun-cc-pVDZ for orientation **T2**.

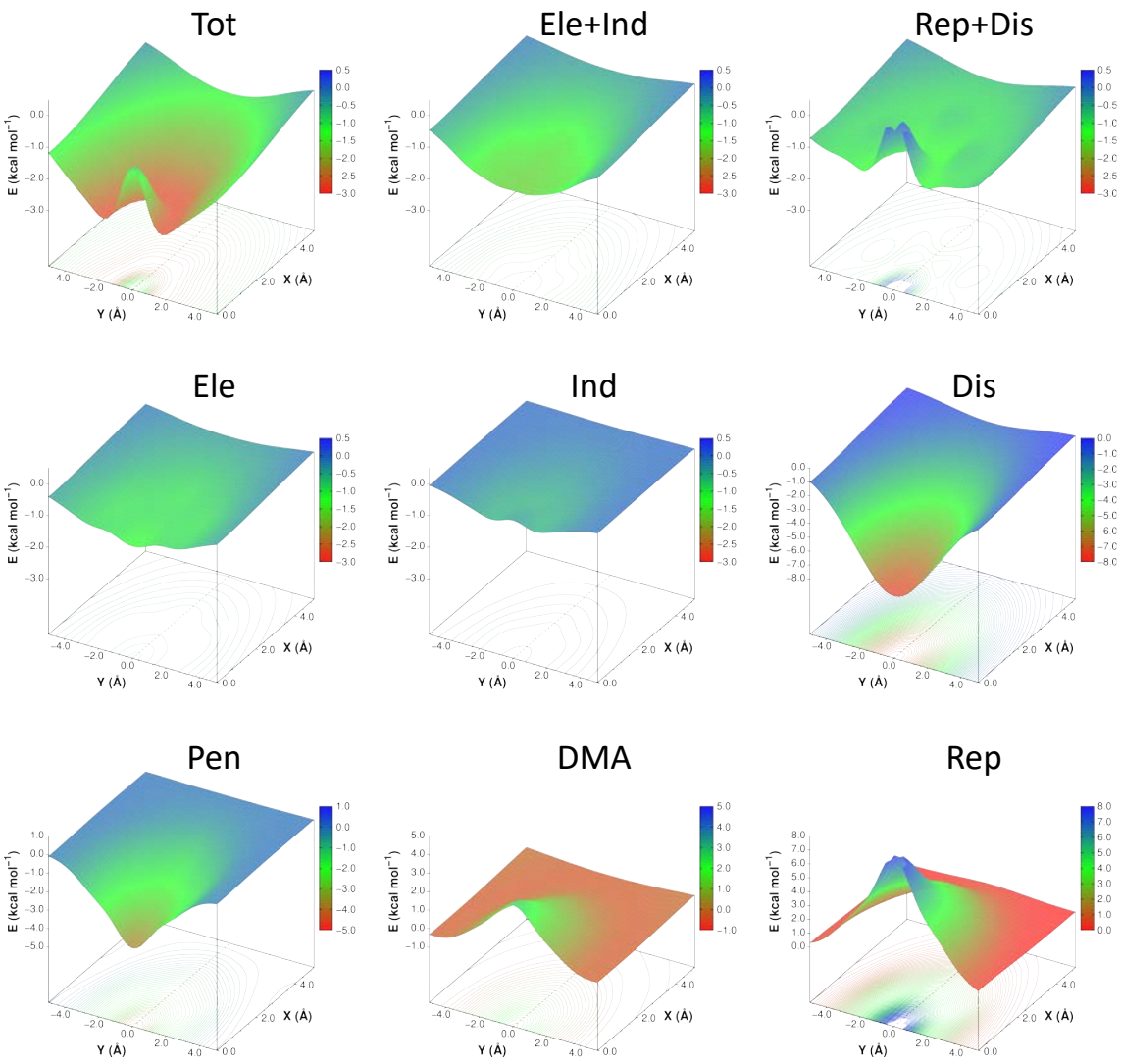


Figure S2. 3D plots of the different contributions to the interaction energy in benzene dimer in parallel stacked orientation. R_v = 3.6 Å.

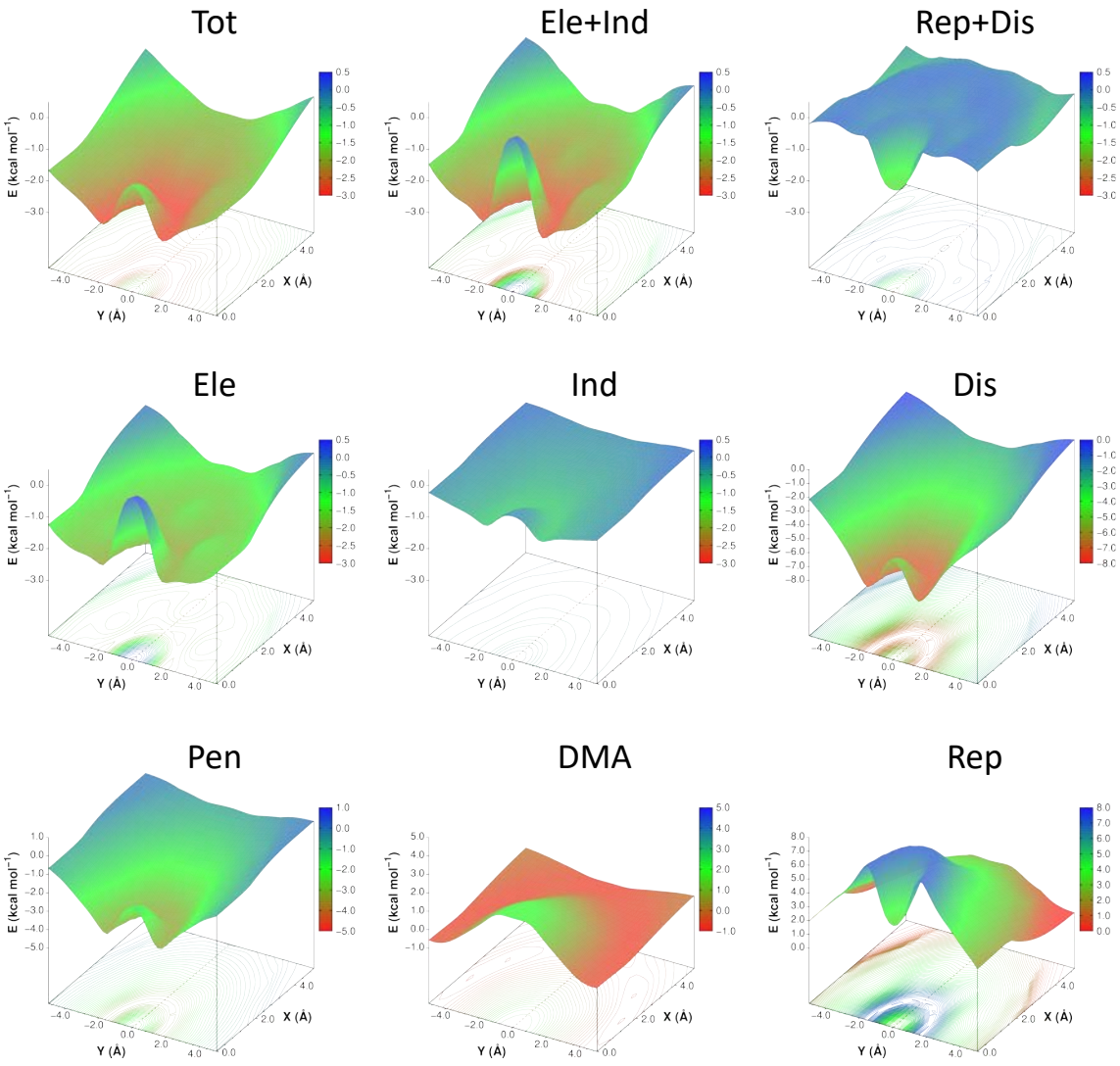


Figure S3. 3D plots of the different contributions to the interaction energy in benzene dimer in parallel stacked orientation. $R_v = R_{v,opt}$.

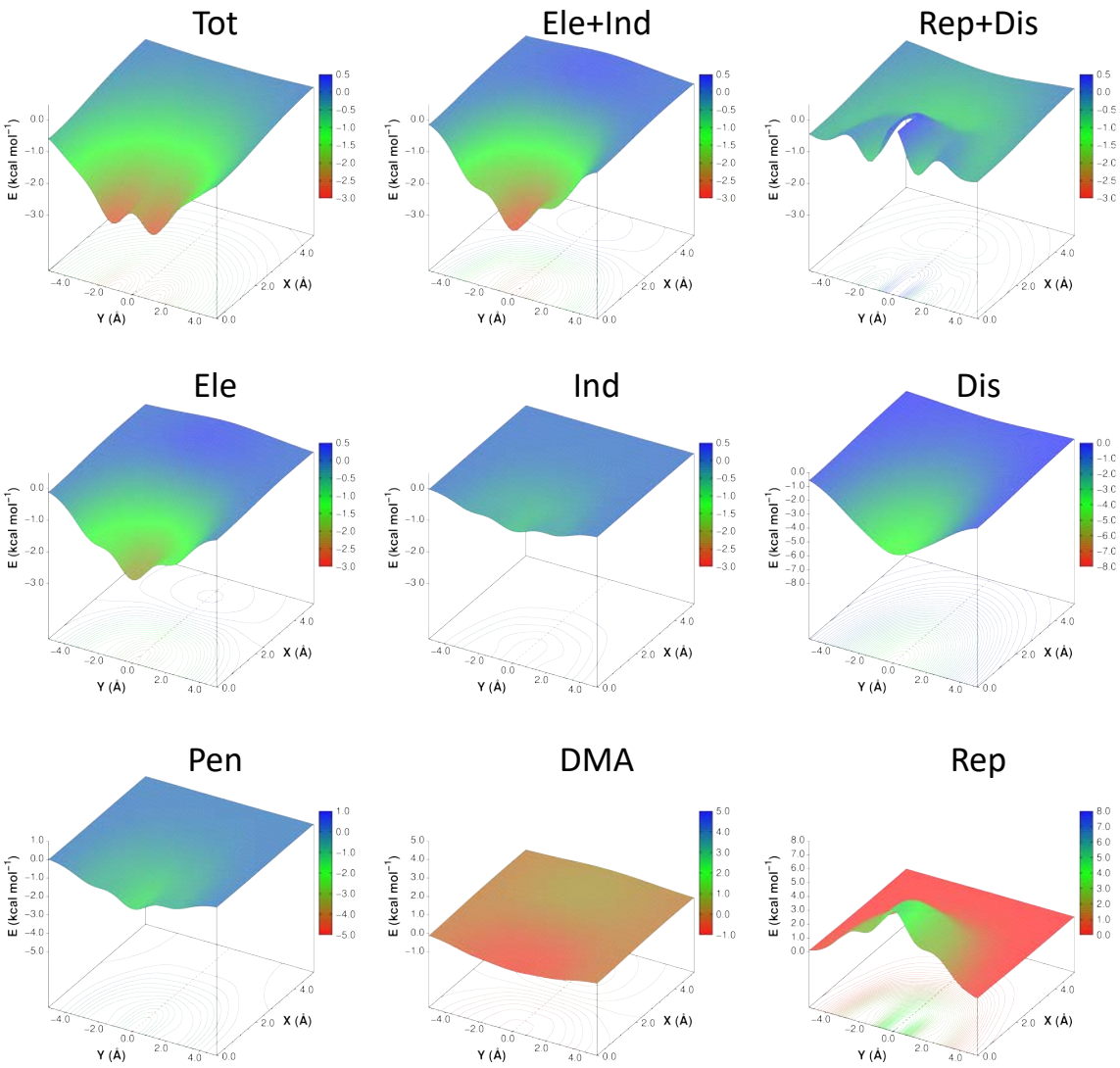


Figure S4. 3D plots of the different contributions to the interaction energy in benzene dimer in T-shaped orientation. R_v = 4.9 Å.

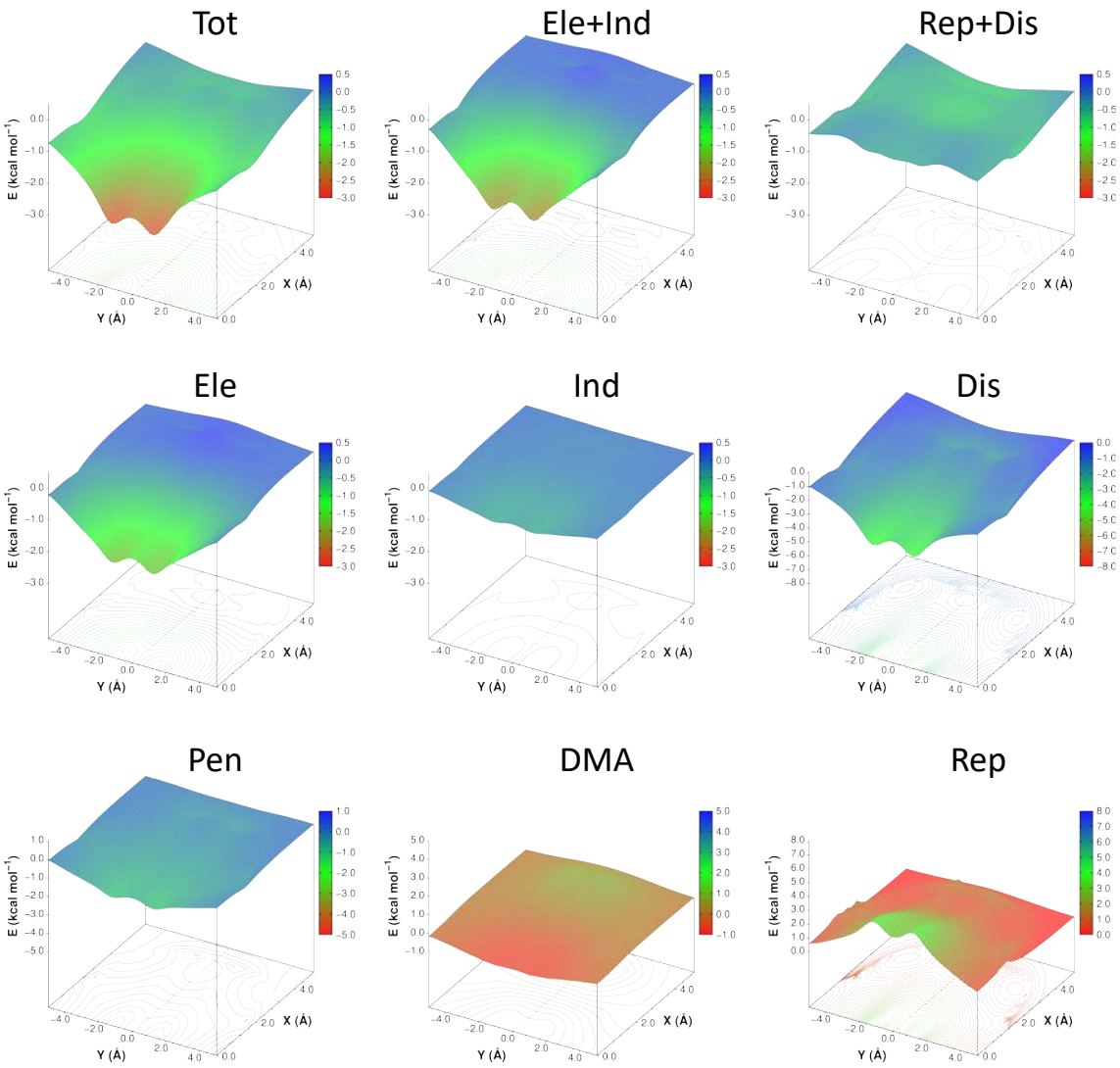


Figure S5. 3D plots of the different contributions to the interaction energy in benzene dimer in T-shaped orientation. $R_v = R_{v,opt}$.

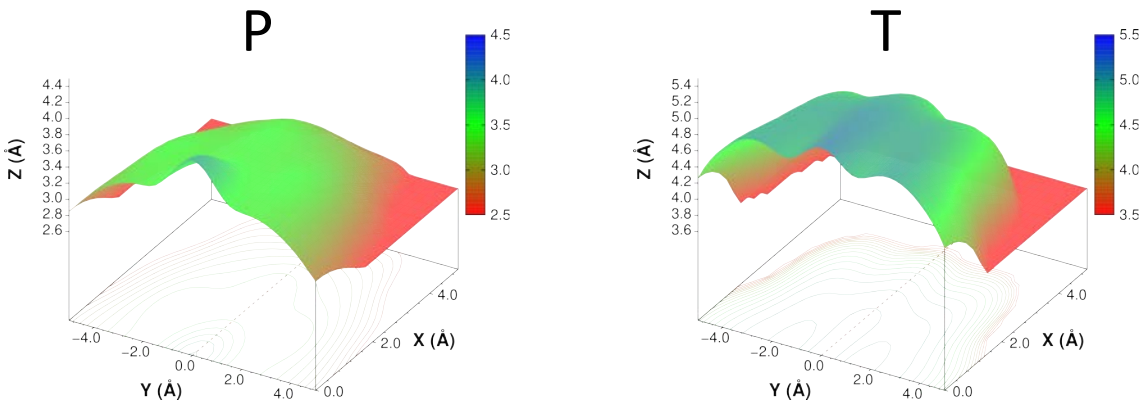


Figure S6. Optimal vertical displacement for benzene dimers. The Y axis passes through two *para* carbon atoms.

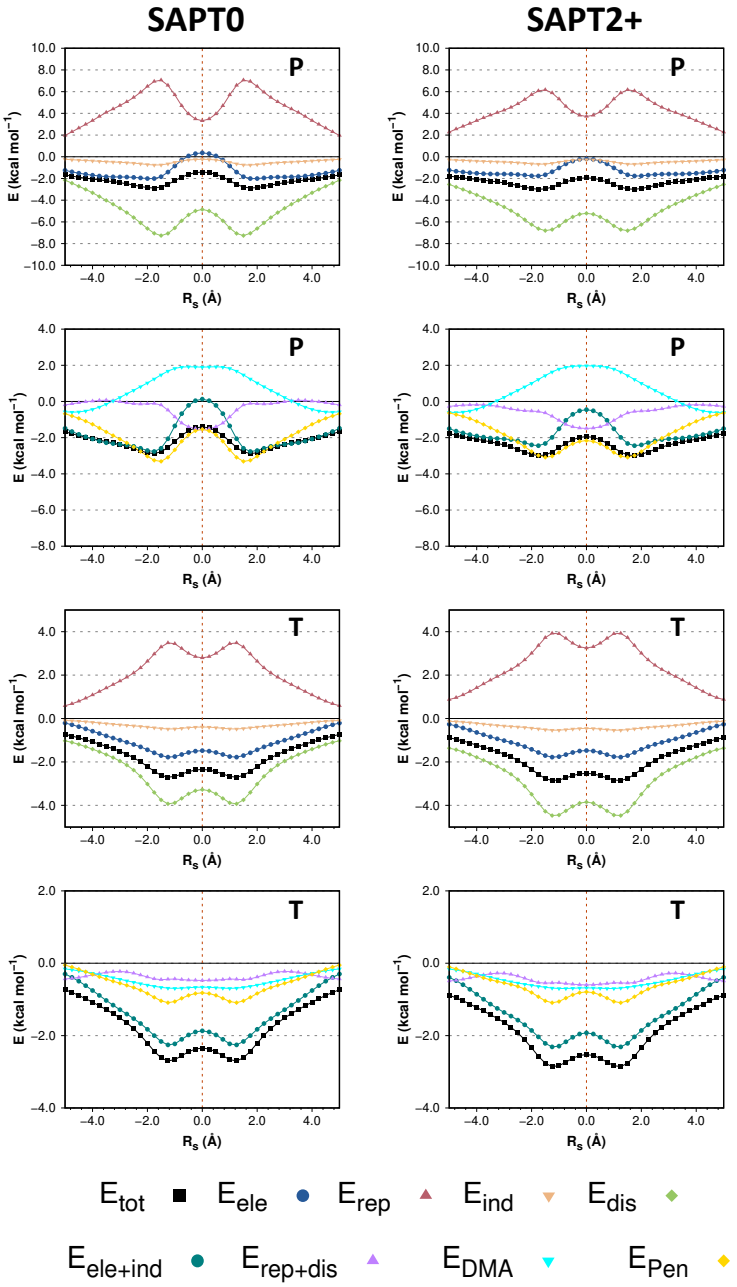


Figure S7. Comparison between the results obtained for benzene dimers at the SAPT0/jun-cc-pVDZ and SAPT2+/aug-cc-pvDZ levels. E_{DMA} in SAPT2+ obtained with distributed multipoles at the MP2/aug-cc-pVDZ level.

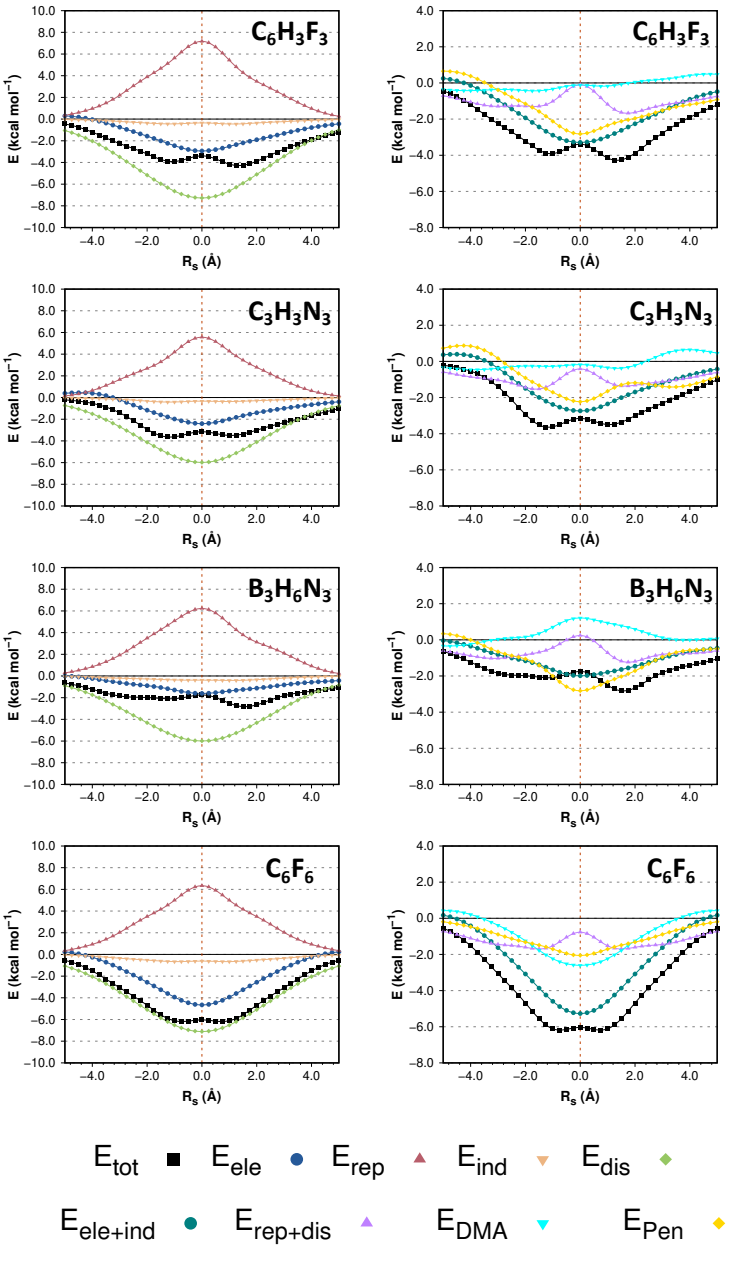


Figure S8. Potential energy curves for parallel heterodimers. R_v = 3.6 Å.

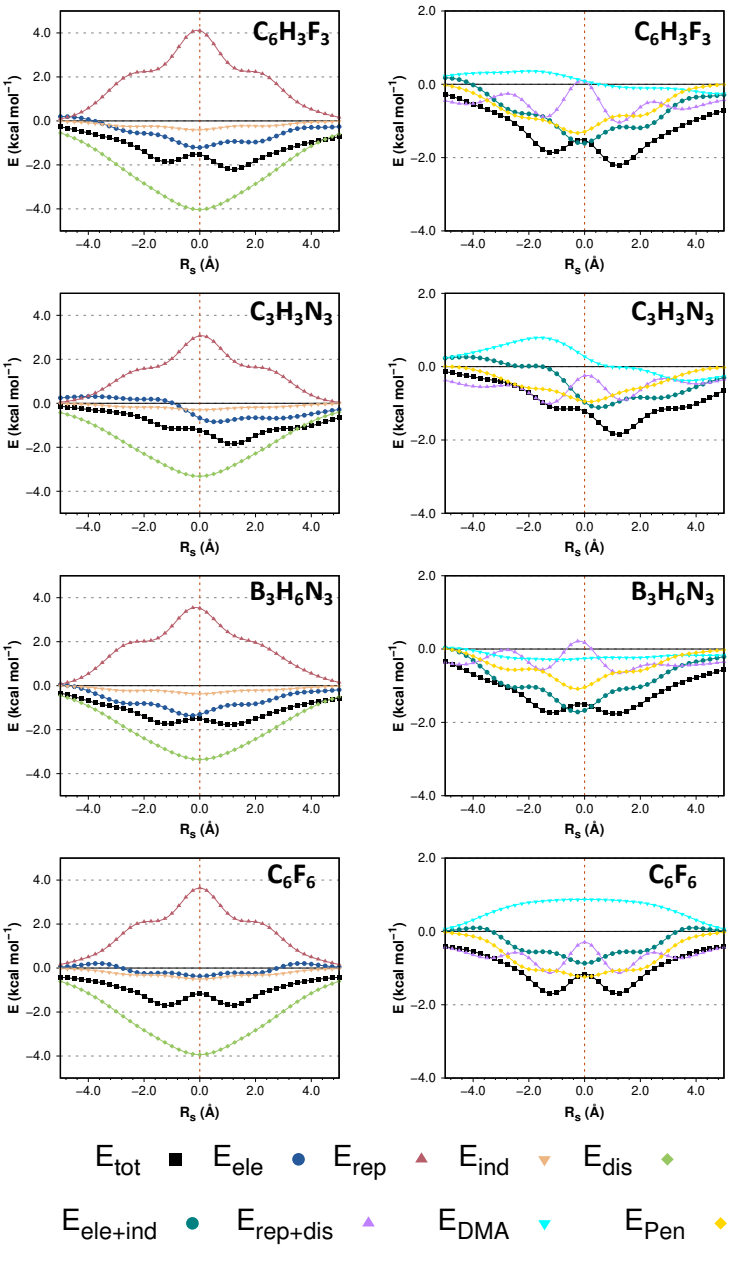


Figure S9. Potential energy curves for T-shaped heterodimers. R_v = 4.9 Å.

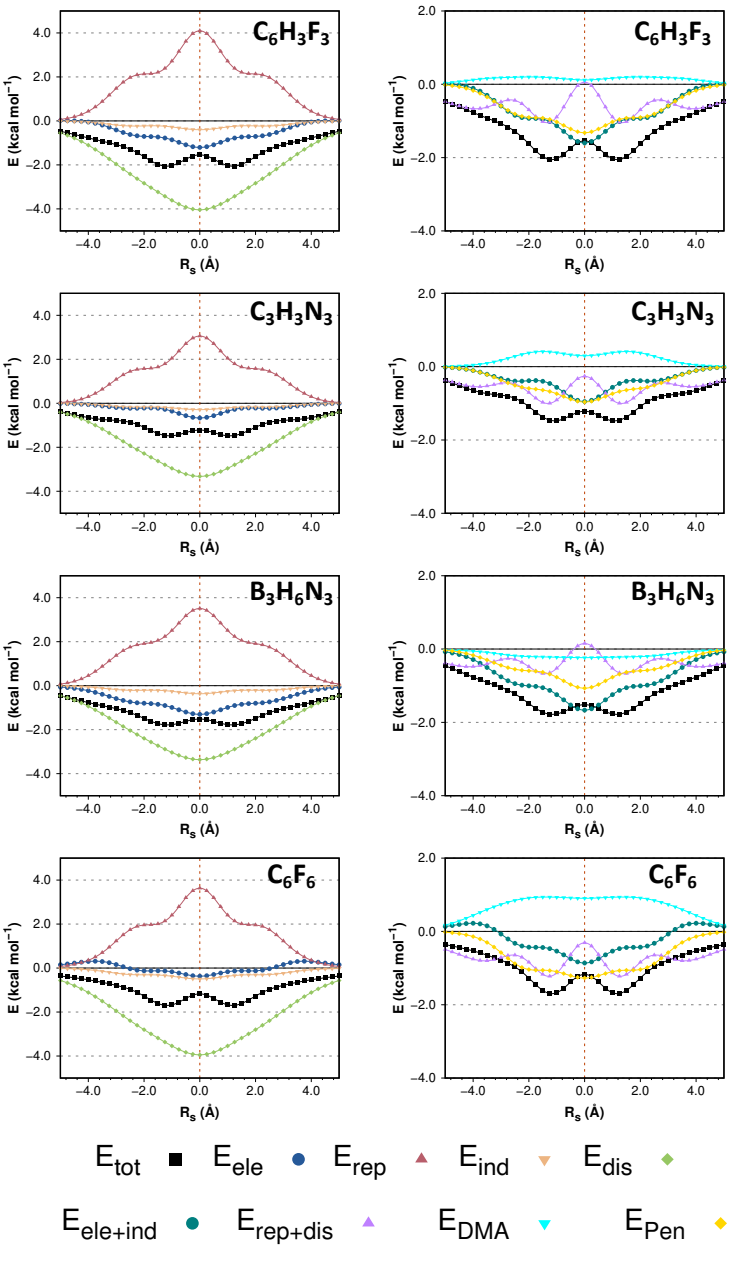


Figure S10. Potential energy curves for T2 heterodimers. R_v = 4.9 Å.

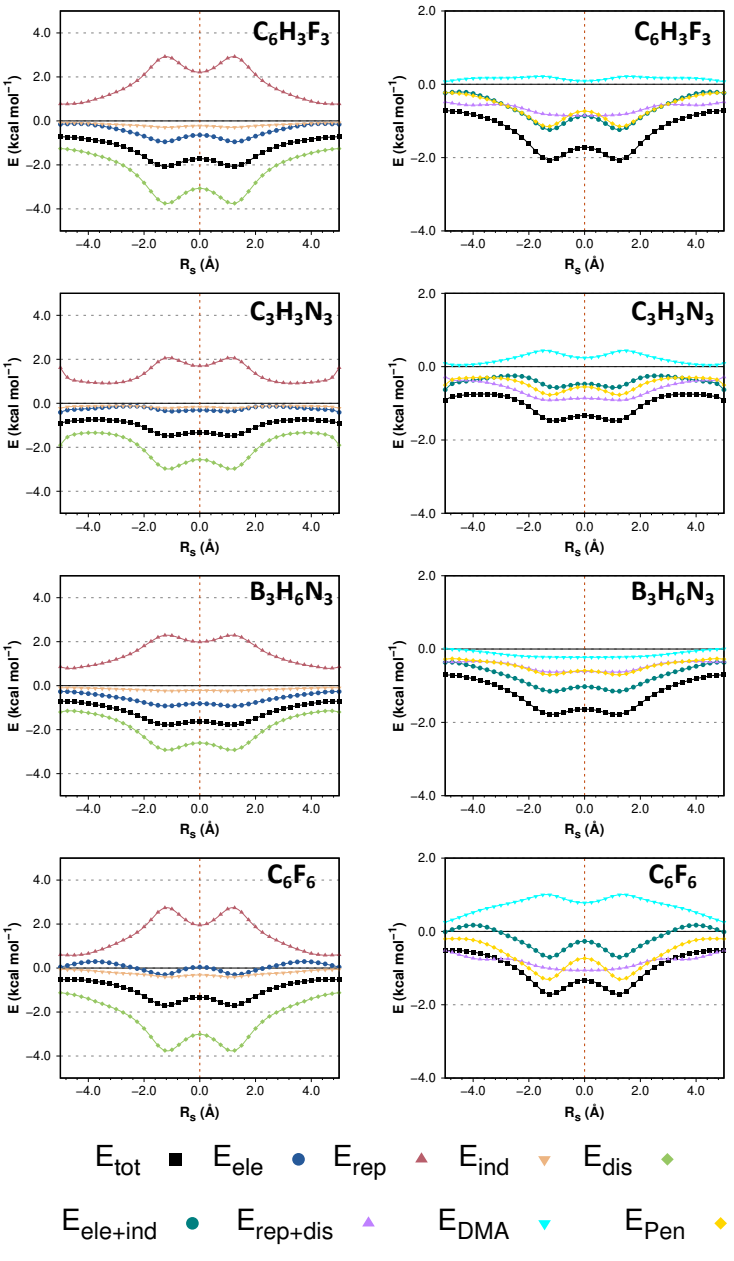


Figure S11. Potential energy curves for T2 heterodimers. R_v = opt.

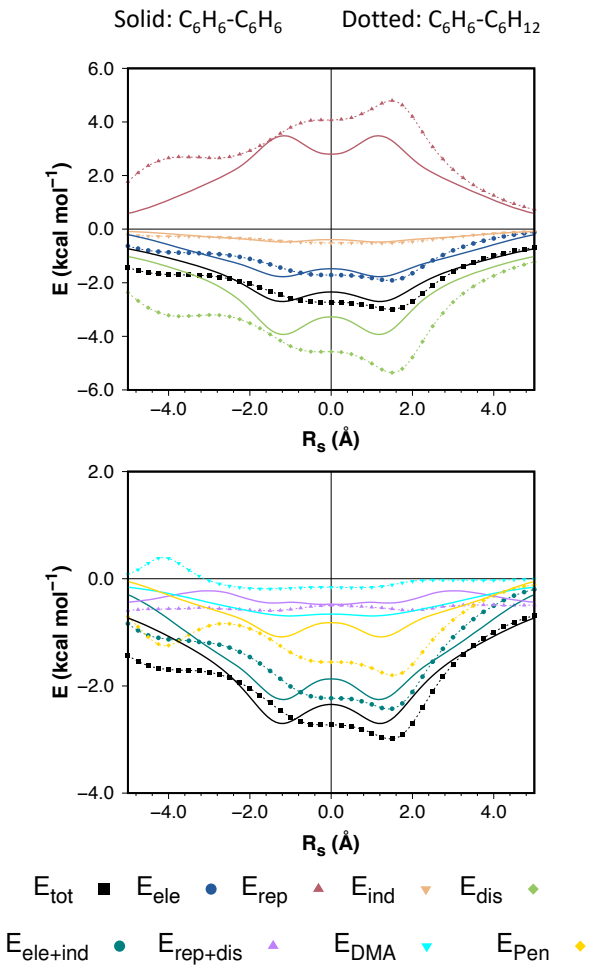


Figure S12. Comparison between T-shaped benzene dimer (solid) and parallel benzene-cyclohexane dimer (dotted).

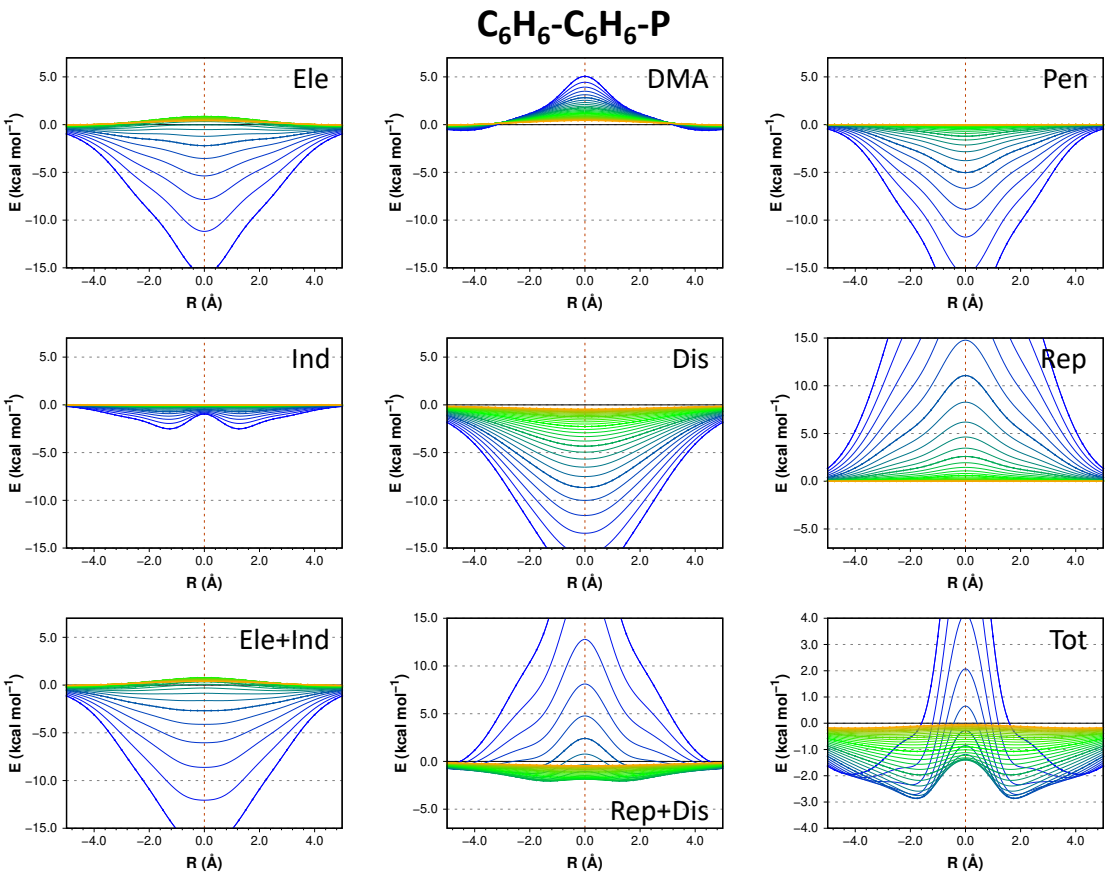


Figure S13. Potential energy curves. Curves start at 3.0 Å; each line corresponds to a 0.1 Å increment, with thick line every 0.5 Å. Colour running from blue to orange).

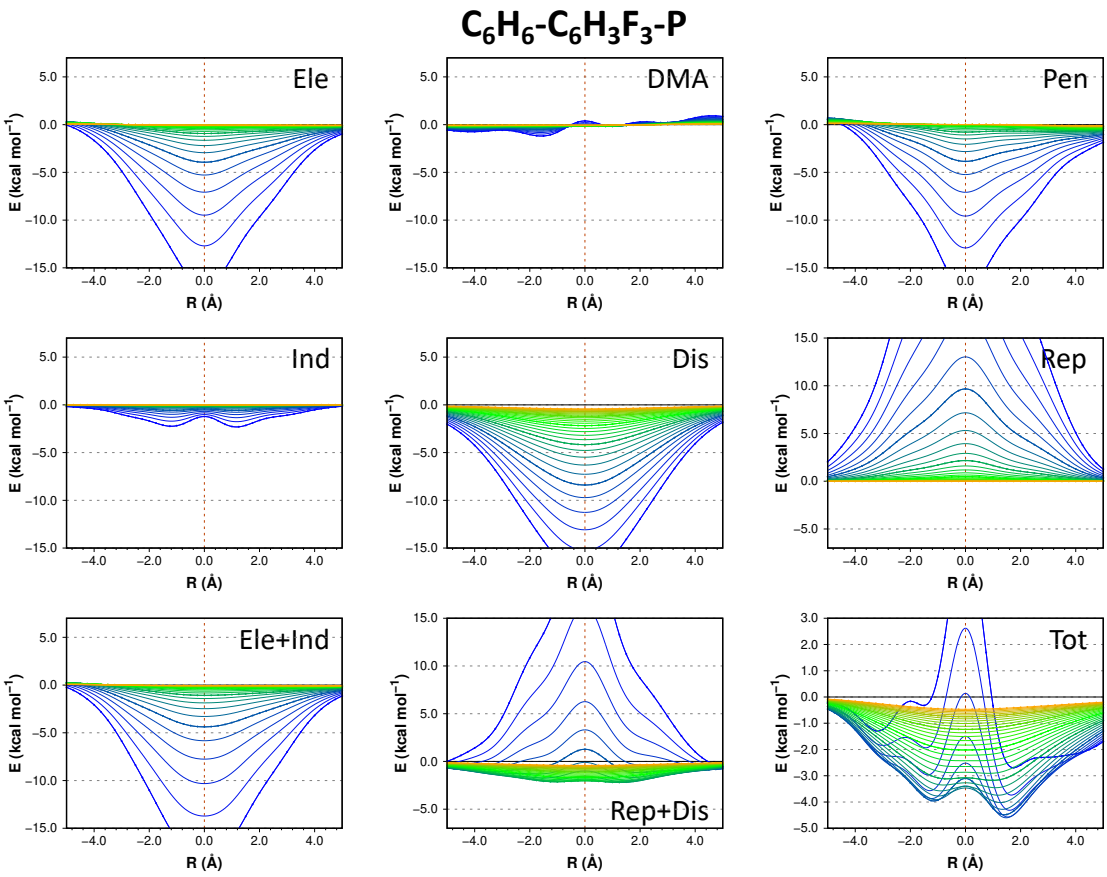


Figure S14. Potential energy curves. Curves start at 3.0 Å; each line corresponds to a 0.1 Å increment, with thick line every 0.5 Å. Colour running from blue to orange).

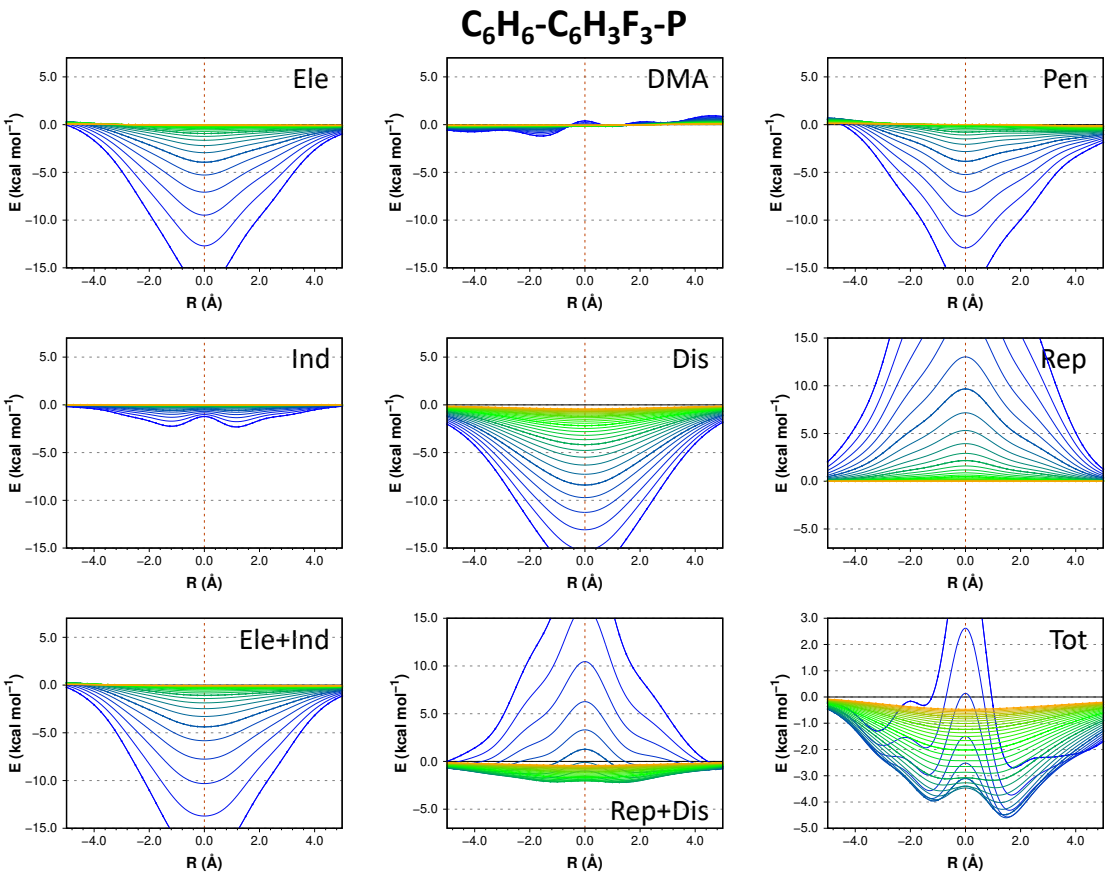


Figure S15. Potential energy curves. Curves start at 3.0 Å; each line corresponds to a 0.1 Å increment, with thick line every 0.5 Å. Colour running from blue to orange).

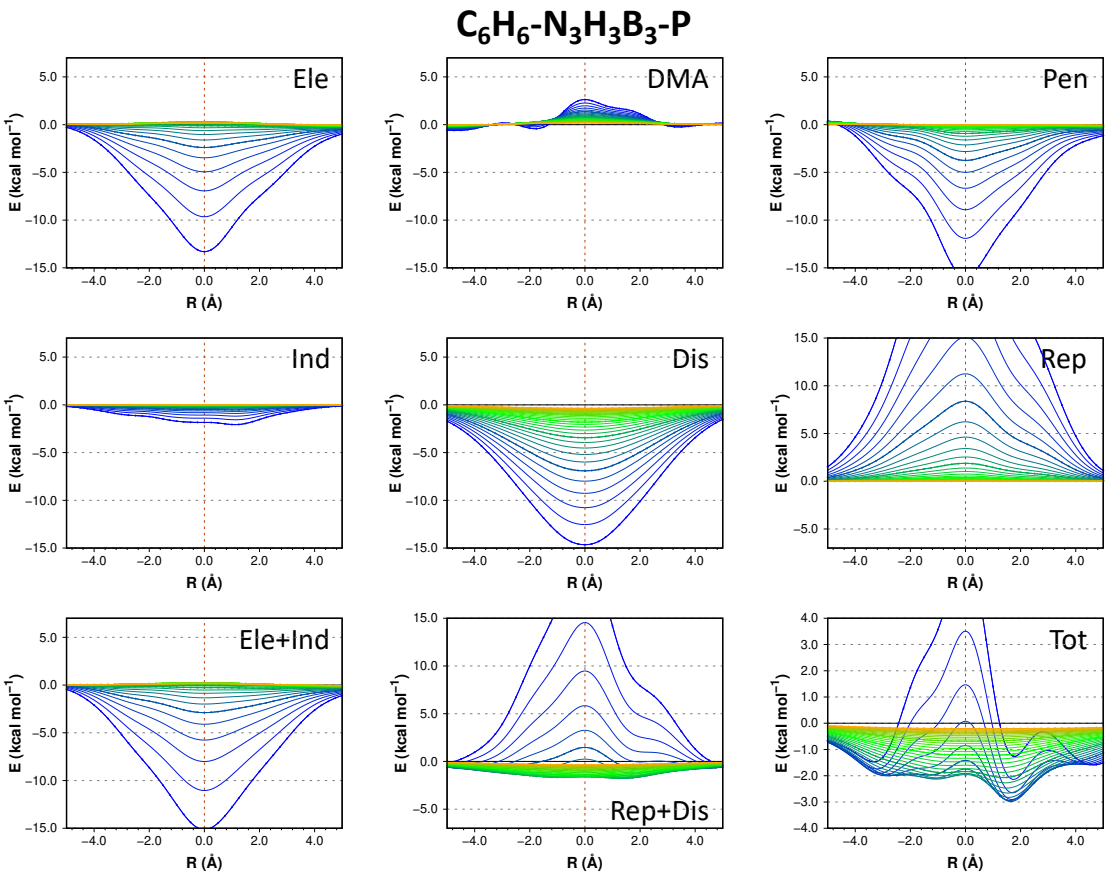


Figure S16. Potential energy curves. Curves start at 3.0 Å; each line corresponds to a 0.1 Å increment, with thick line every 0.5 Å. Colour running from blue to orange).

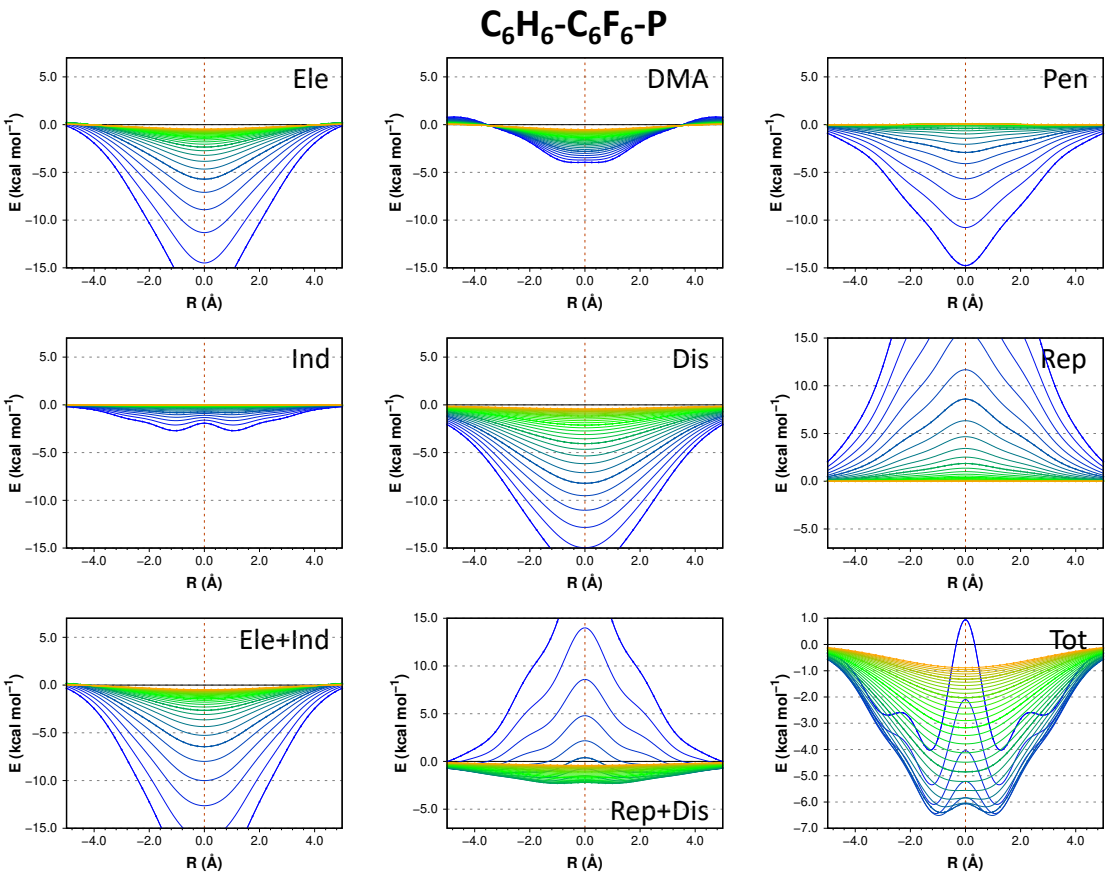


Figure S17. Potential energy curves. Curves start at 3.0 Å; each line corresponds to a 0.1 Å increment, with thick line every 0.5 Å. Colour running from blue to orange).

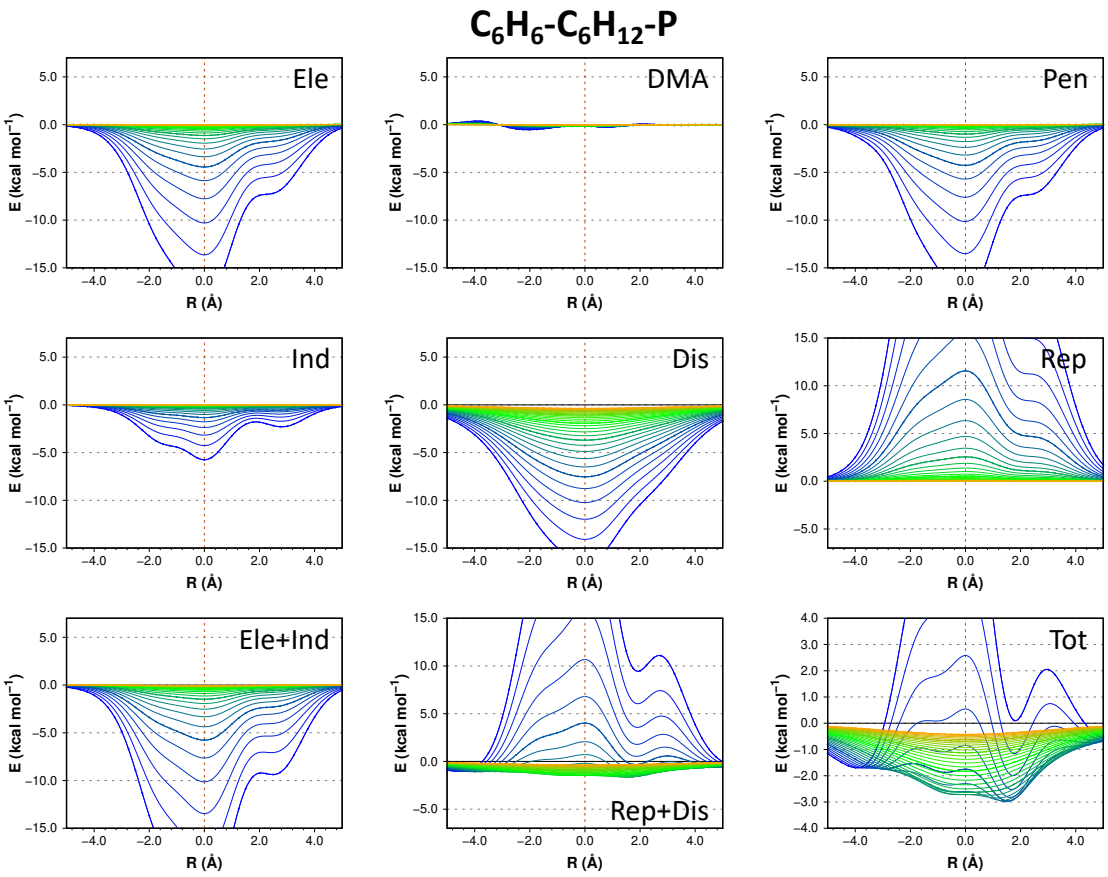


Figure S18. Potential energy curves. Curves start at 3.5 Å; each line corresponds to a 0.1 Å increment, with thick line every 0.5 Å. Colour running from blue to orange).

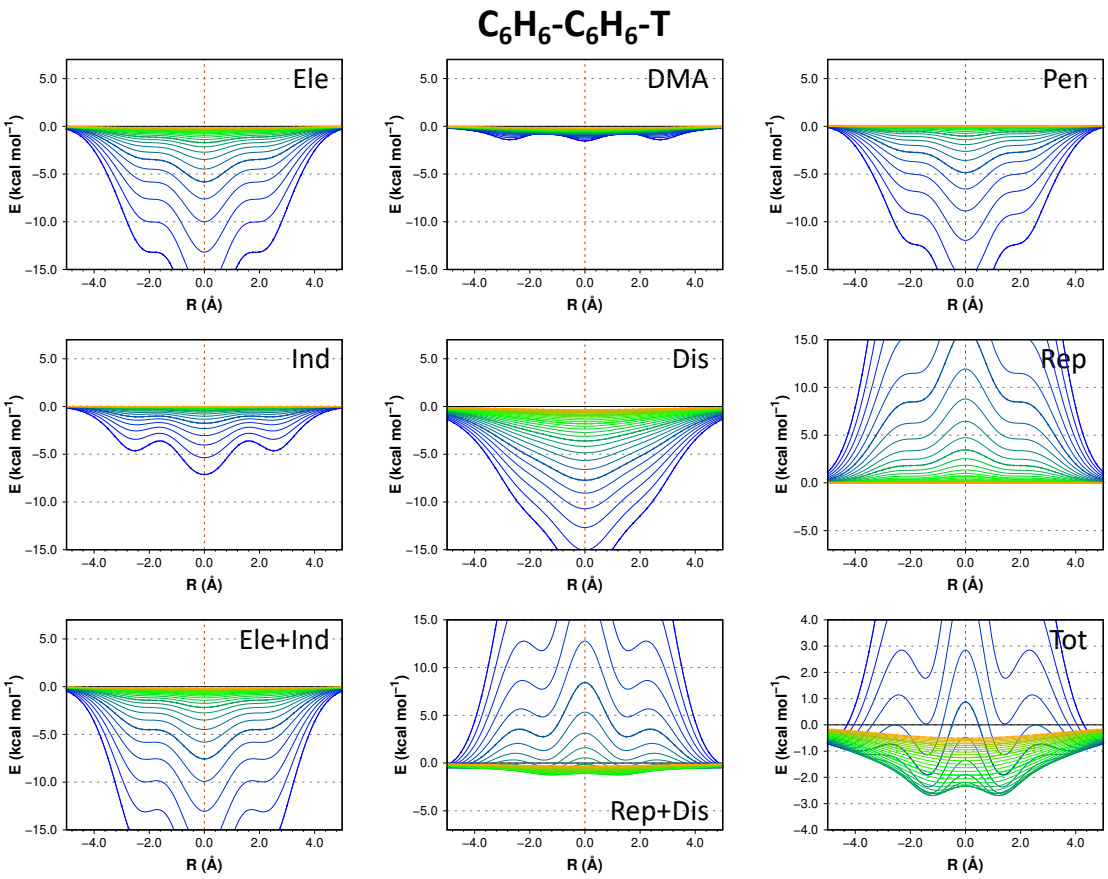


Figure S19. Potential energy curves. Curves start at 4.0 Å; each line corresponds to a 0.1 Å increment, with thick line every 0.5 Å. Colour running from blue to orange).

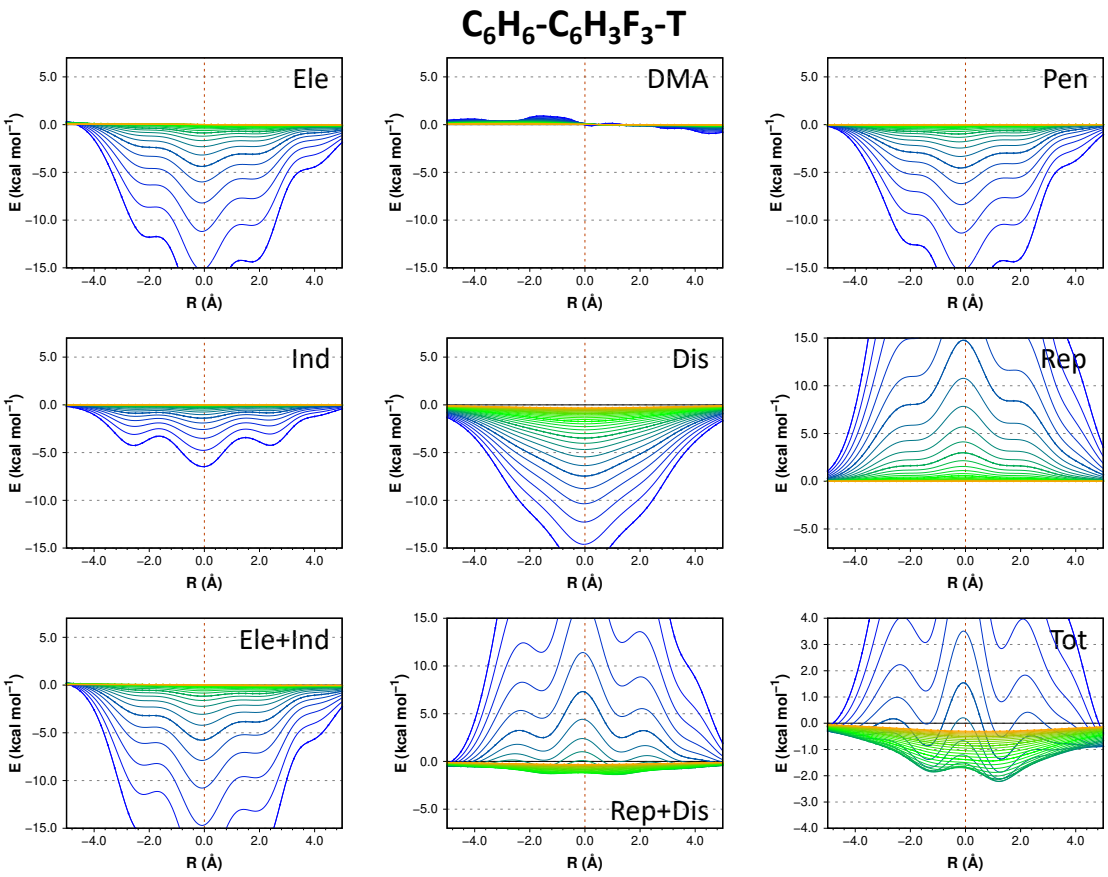


Figure S20. Potential energy curves. Curves start at 4.0 Å; each line corresponds to a 0.1 Å increment, with thick line every 0.5 Å. Colour running from blue to orange).

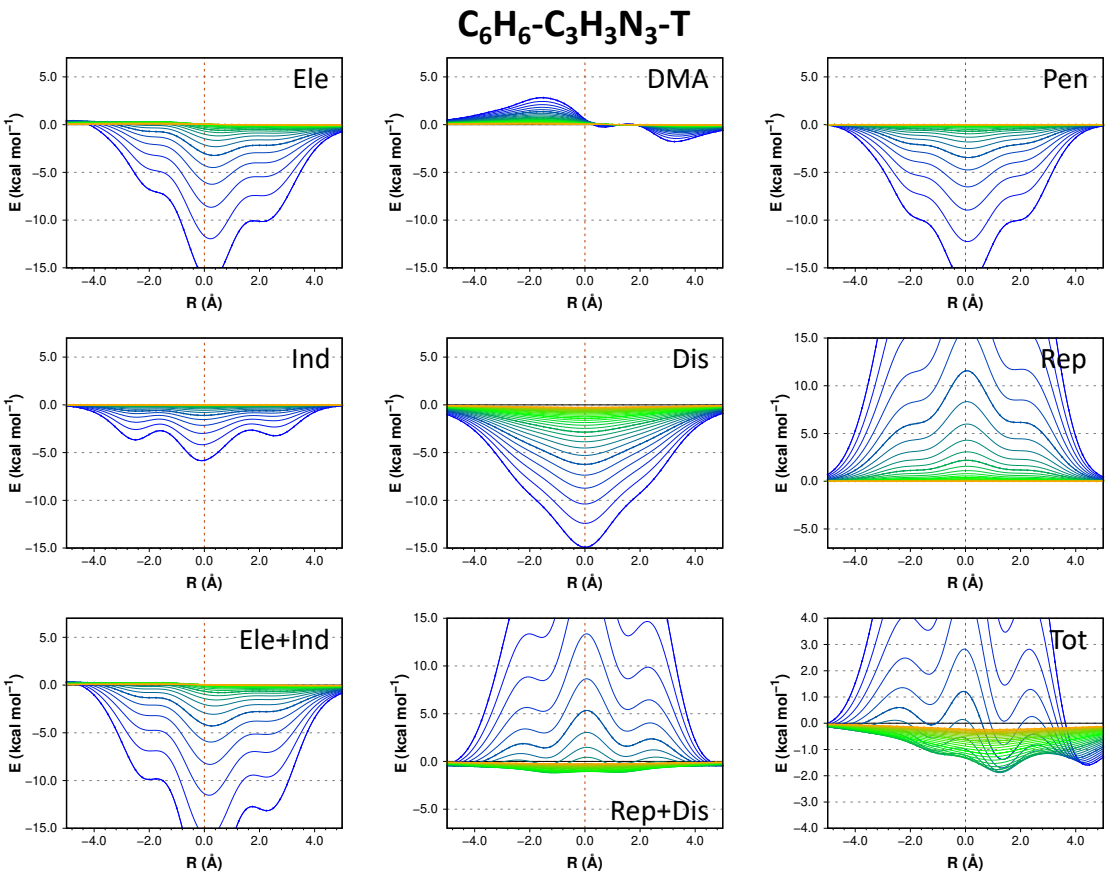


Figure S21. Potential energy curves. Curves start at 4.0 Å; each line corresponds to a 0.1 Å increment, with thick line every 0.5 Å. Colour running from blue to orange).

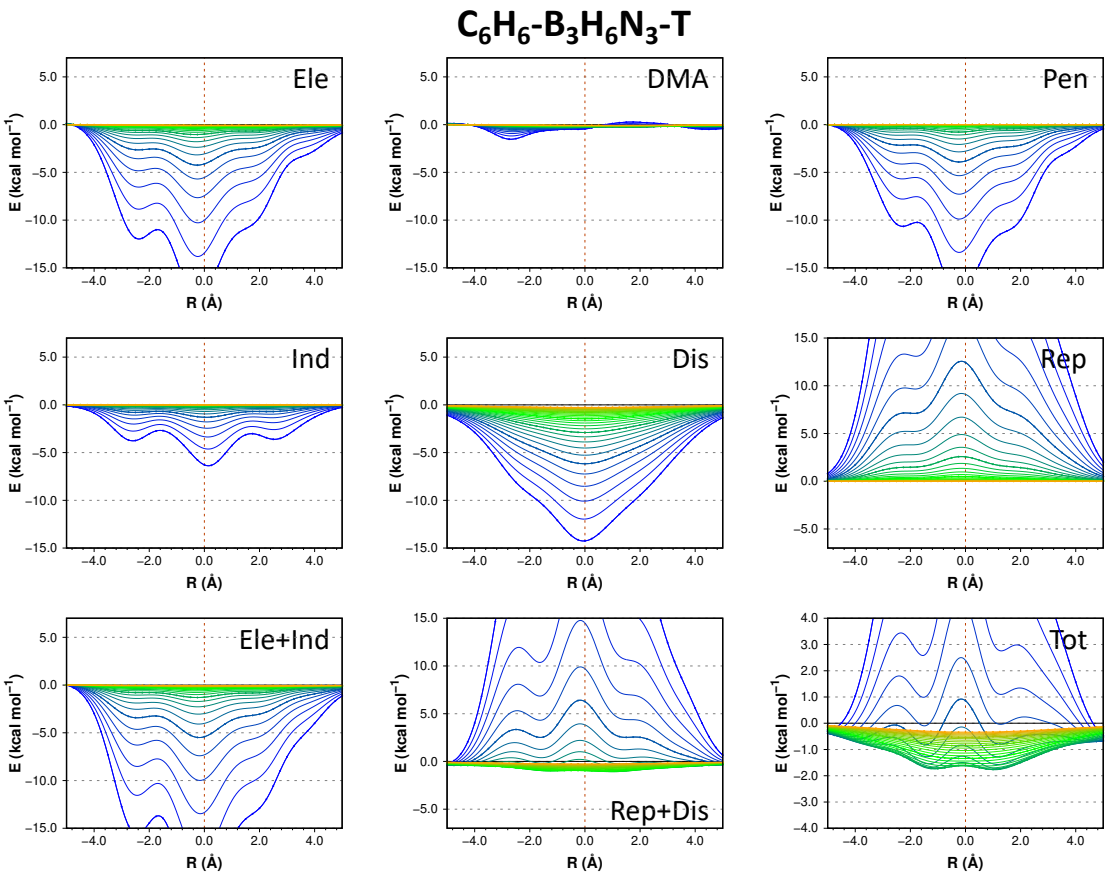


Figure S22. Potential energy curves. Curves start at 4.0 Å; each line corresponds to a 0.1 Å increment, with thick line every 0.5 Å. Colour running from blue to orange).

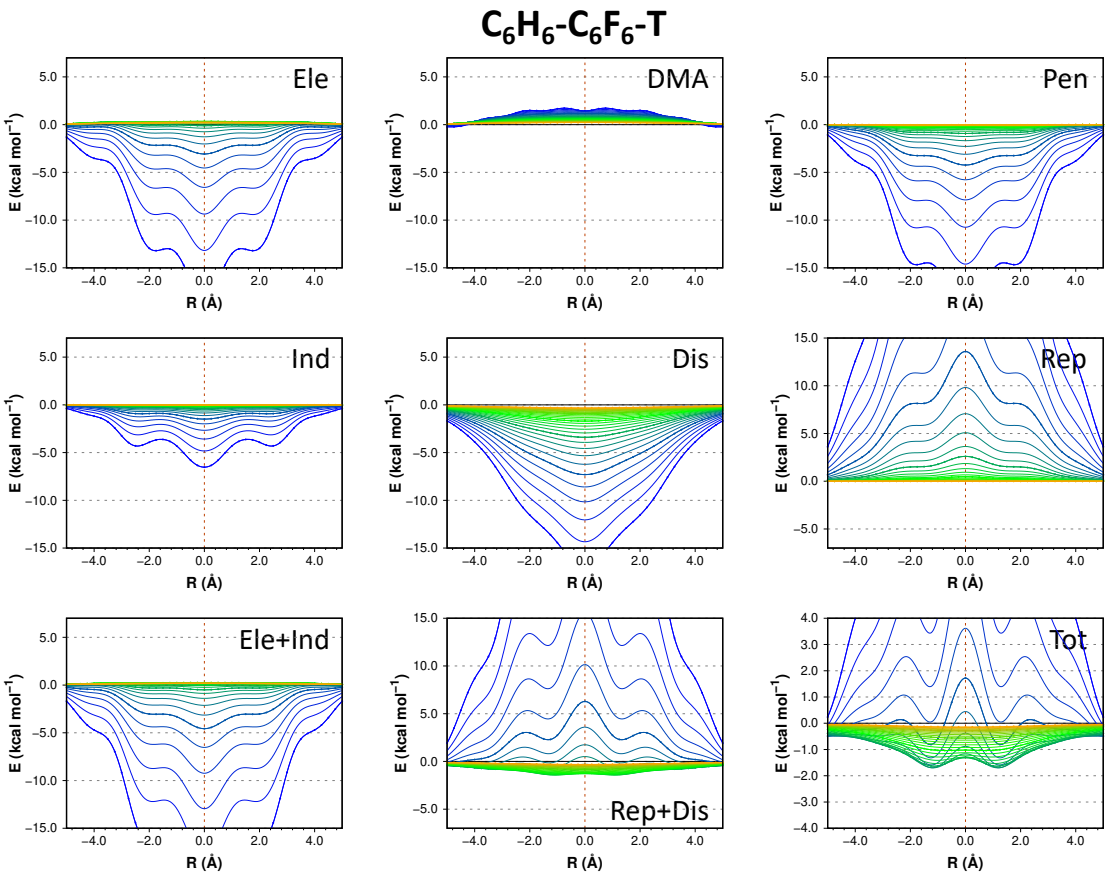


Figure S23. Potential energy curves. Curves start at 4.0 Å; each line corresponds to a 0.1 Å increment, with thick line every 0.5 Å. Colour running from blue to orange).

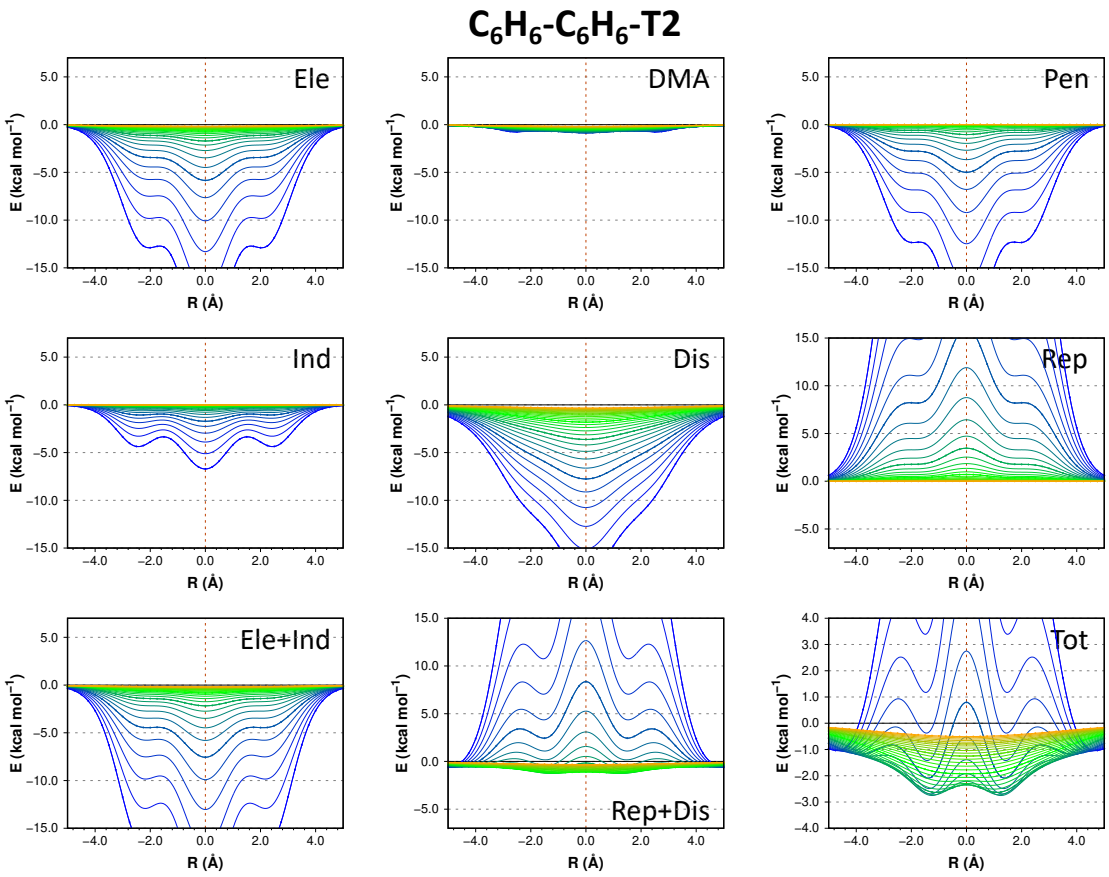


Figure S24. Potential energy curves. Curves start at 4.0 Å; each line corresponds to a 0.1 Å increment, with thick line every 0.5 Å. Colour running from blue to orange).

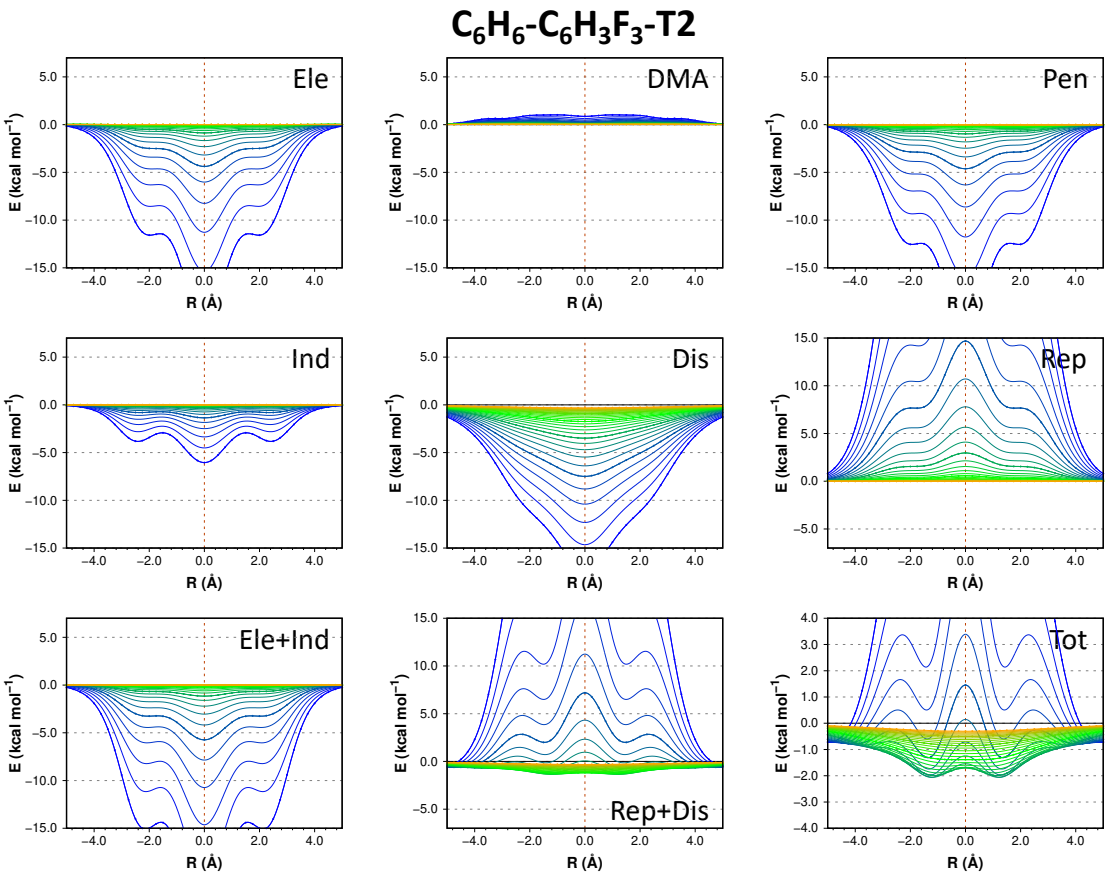


Figure S25. Potential energy curves. Curves start at 4.0 Å; each line corresponds to a 0.1 Å increment, with thick line every 0.5 Å. Colour running from blue to orange).

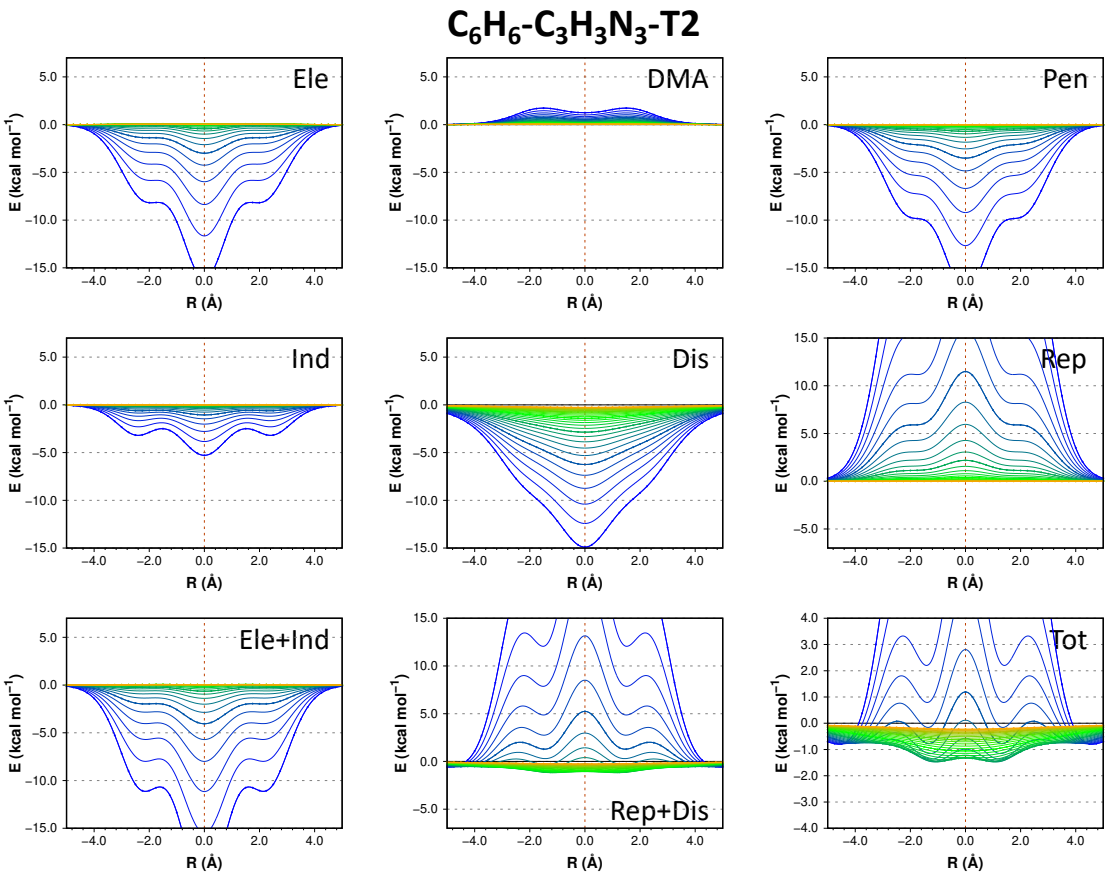


Figure S26. Potential energy curves. Curves start at 4.0 Å; each line corresponds to a 0.1 Å increment, with thick line every 0.5 Å. Colour running from blue to orange).

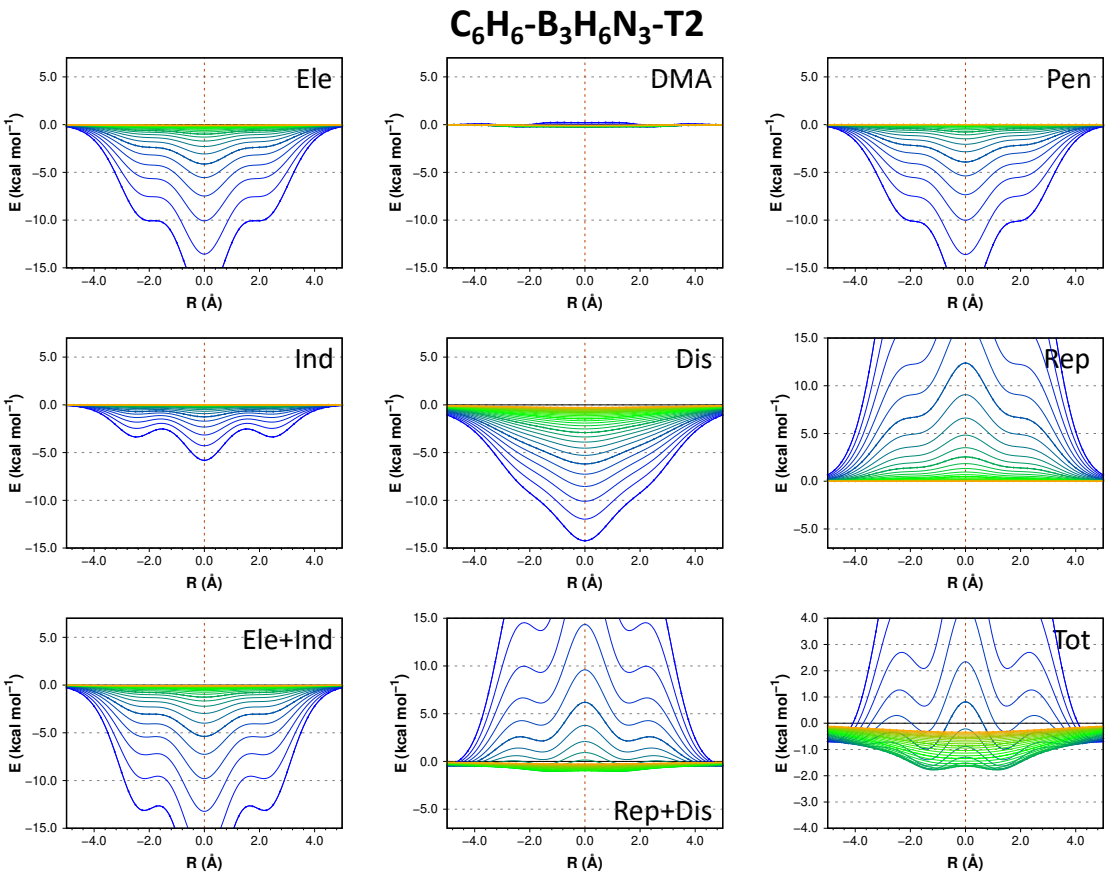


Figure S27. Potential energy curves. Curves start at 4.0 Å; each line corresponds to a 0.1 Å increment, with thick line every 0.5 Å. Colour running from blue to orange).

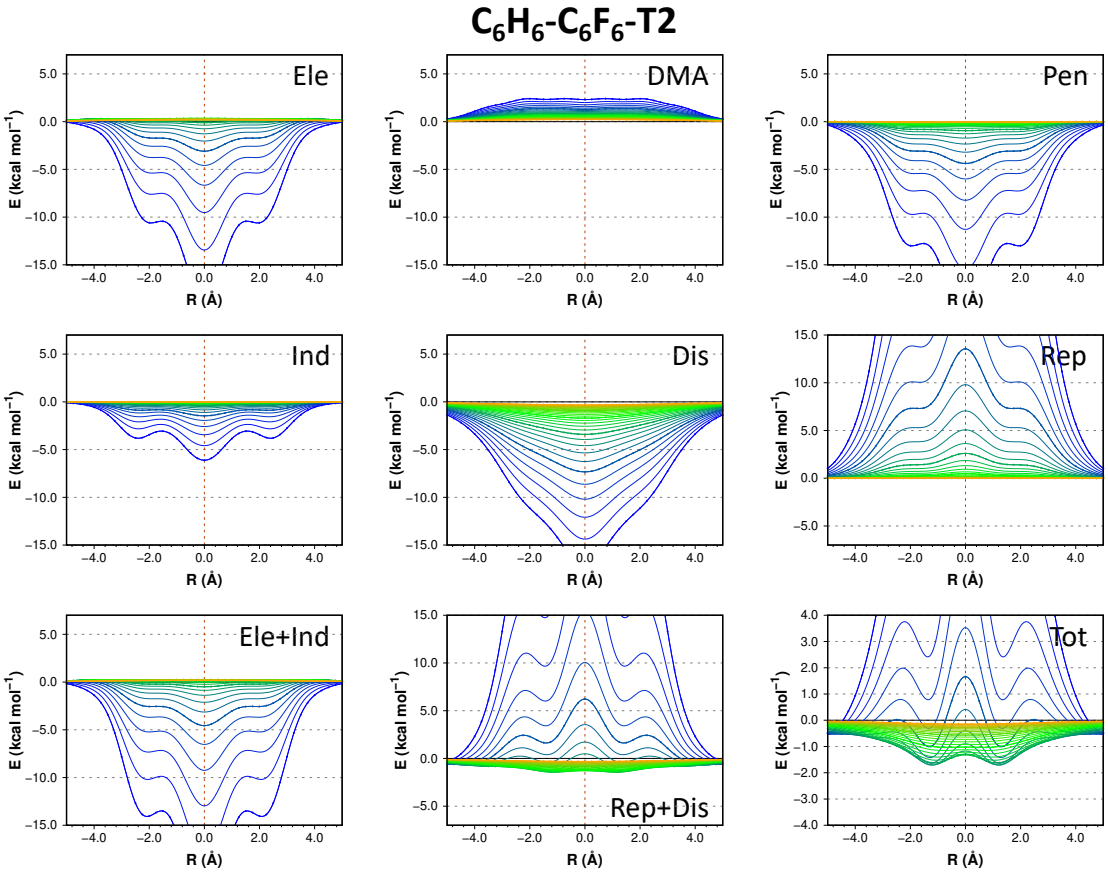


Figure S28. Potential energy curves. Curves start at 4.0 Å; each line corresponds to a 0.1 Å increment, with thick line every 0.5 Å. Colour running from blue to orange).

Cartesian coordinates (Å) for the optimised structures of the molecules employed in this study at the B3LYP/def2-TZVPP level.

Benzene

C	1.2049982772	-0.6957060797	0.0000000000
C	1.2049982772	0.6957060797	0.0000000000
C	0.0000000000	1.3914121594	0.0000000000
C	-1.2049982772	0.6957060797	0.0000000000
C	-1.2049982772	-0.6957060797	0.0000000000
C	0.0000000000	-1.3914121594	0.0000000000
H	2.1424917818	-1.2369682069	0.0000000000
H	2.1424917818	1.2369682069	0.0000000000
H	0.0000000000	2.4739364139	0.0000000000
H	-2.1424917818	1.2369682069	0.0000000000
H	-2.1424917818	-1.2369682069	0.0000000000
H	0.0000000000	-2.4739364139	0.0000000000

Trifluorobenzene

C	1.1800748486	-0.6813165315	0.0000000000
C	1.2179636166	0.7031916219	0.0000000000
C	0.0000000000	1.3626330630	0.0000000000
C	-1.2179636166	0.7031916219	0.0000000000
C	-1.1800748486	-0.6813165315	0.0000000000
C	0.0000000000	-1.4063832438	0.0000000000
F	2.3445631928	-1.3536341905	0.0000000000
H	2.1526636276	1.2428409249	0.0000000000
F	0.0000000000	2.7072683810	0.0000000000
H	-2.1526636276	1.2428409249	0.0000000000
F	-2.3445631928	-1.3536341905	0.0000000000
H	0.0000000000	-2.4856818497	0.0000000000

Triazine

N	1.1840888049	-0.6836339903	0.0000000000
C	1.1188225182	0.6459524821	0.0000000000
N	0.0000000000	1.3672679805	0.0000000000
C	-1.1188225182	0.6459524821	0.0000000000
N	-1.1840888049	-0.6836339903	0.0000000000
C	0.0000000000	-1.2919049641	0.0000000000
H	2.0583294801	1.1883770794	0.0000000000
H	-2.0583294801	1.1883770794	0.0000000000
H	0.0000000000	-2.3767541588	0.0000000000

Borazine

B	1.2553164694	-0.7247573015	0.0000000000
N	1.2186487370	0.7035871763	0.0000000000
B	0.0000000000	1.4495146030	0.0000000000
N	-1.2186487370	0.7035871763	0.0000000000
B	-1.2553164694	-0.7247573015	0.0000000000
N	0.0000000000	-1.4071743527	0.0000000000
H	2.2877281253	-1.3208204490	0.0000000000
H	2.0902466649	1.2068044747	0.0000000000
H	0.0000000000	2.6416408979	0.0000000000
H	-2.0902466649	1.2068044747	0.0000000000
H	-2.2877281253	-1.3208204490	0.0000000000
H	0.0000000000	-2.4136089493	0.0000000000

Hexafluorobenzene

C	1.2028844968	-0.6944856880	0.0000000000
C	1.2028844968	0.6944856880	0.0000000000
C	0.0000000000	1.3889713760	0.0000000000
C	-1.2028844968	0.6944856880	0.0000000000
C	-1.2028844968	-0.6944856880	0.0000000000
C	0.0000000000	-1.3889713760	0.0000000000
F	2.3563340573	-1.3604301023	0.0000000000
F	2.3563340573	1.3604301023	0.0000000000
F	0.0000000000	2.7208602045	0.0000000000
F	-2.3563340573	1.3604301023	0.0000000000
F	-2.3563340573	-1.3604301023	0.0000000000
F	0.0000000000	-2.7208602045	0.0000000000

Cyclohexane

C	-1.2677006138	0.7319072906	-0.2271542664
C	-1.2677006138	-0.7319072906	0.2271542664
C	0.0000000000	1.4638145812	0.2271542664
C	0.0000000000	-1.4638145812	-0.2271542664
C	1.2677006138	0.7319072906	-0.2271542664
C	1.2677006138	-0.7319072906	0.2271542664
H	-2.1557785331	1.2446393164	0.1510013005
H	-2.1557785331	-1.2446393164	-0.1510013005
H	-1.3309387475	0.7684178442	-1.3205955823
H	-1.3309387475	-0.7684178442	1.3205955823
H	0.0000000000	1.5368356883	1.3205955823
H	0.0000000000	-1.5368356883	-1.3205955823
H	0.0000000000	2.4892786328	-0.1510013005
H	0.0000000000	-2.4892786328	0.1510013005
H	1.3309387475	0.7684178442	-1.3205955823
H	1.3309387475	-0.7684178442	1.3205955823
H	2.1557785331	1.2446393164	0.1510013005
H	2.1557785331	-1.2446393164	-0.1510013005