Supporting Information

BENCHMARK CALCULATIONS

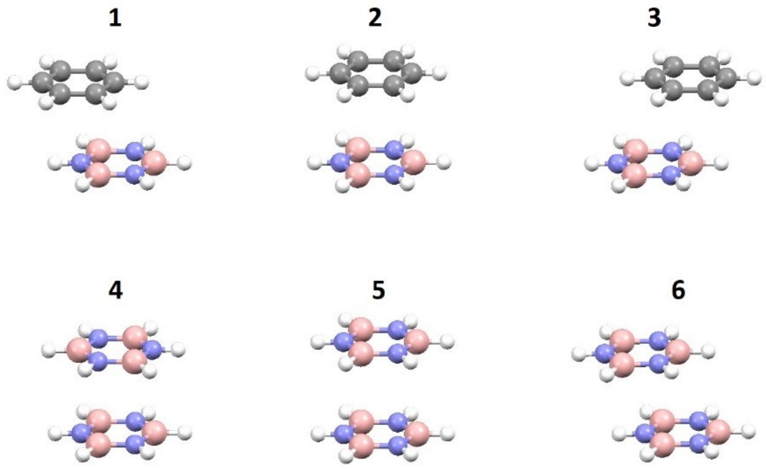

Figure S1. Three borazine-benzene (1-3) and three borazine-borazine dimers (4-6) used for benchmark calculations.

Table S1. Geometrical parameters and interaction energies for selected orientations in borazine-benzene and borazine-borazine dimers

structure		r [Å]	R [Å]	ΔE CCSD(T)/CBS [kcal/mol]	ΔE B3LYP-D3 def2-TZVP [kcal/mol]	ΔE B3LYP-D3BJ def2-TZVP [kcal/mol]
benzene-borazine	**1**	-1.5	3.5	-2.47	-2.55	-2.82
			3.6	-2.56	-2.58	-2.81
			3.7	-2.51	-2.51	-2.71
	2	0.0	3.7	-2.34	-2.37	-2.61
			3.8	-2.35	-2.35	-2.55
			3.9	-2.30	-2.25	-2.41
	3	+1.5	3.3	-3.18	-3.06	-3.46
			3.4	-3.30	-3.23	-3.56
			3.5	-3.25	-3.23	-3.50
borazine-borazine	**4**	0.0	3.4	-3.48	-3.56	-4.02
			3.5	-3.53	-3.63	-4.01
			3.6	-3.43	-3.54	-3.88
	5	0.0	3.8	-1.88	-1.95	-2.22
			3.9	-1.90	-1.92	-2.13
			4.0	-1.84	-1.84	-2.01
	6	1.5	3.3	-3.02	-2.92	-3.41
			3.4	-3.11	-3.08	-3.47
			3.5	-3.06	-3.06	-3.39

BORAZINE-BENZENE STACKING – MODEL-SYSTEMS AND POTENTIAL ENERGY CURVES

Four model systems were considered for the calculations of borazine-benzene potential energy surfaces (Figure S2). In the first model system, sandwich geometry is *eclipsed* **E** and benzene is displaced *along* the direction of N-H (or B-H) bonds (model system $\mathbf{E_a}$). In the second model system, sandwich geometry is also *eclipsed*, and benzene is displaced in the direction *between* B-N bonds (model system $\mathbf{E_b}$). In the third and fourth model system, sandwich geometry is *staggered*, and benzene is displaced *along* the direction of N-H (or B-H) bonds (model system $\mathbf{S_a}$), or in the direction *between* B-N bonds (model system $\mathbf{S_b}$).

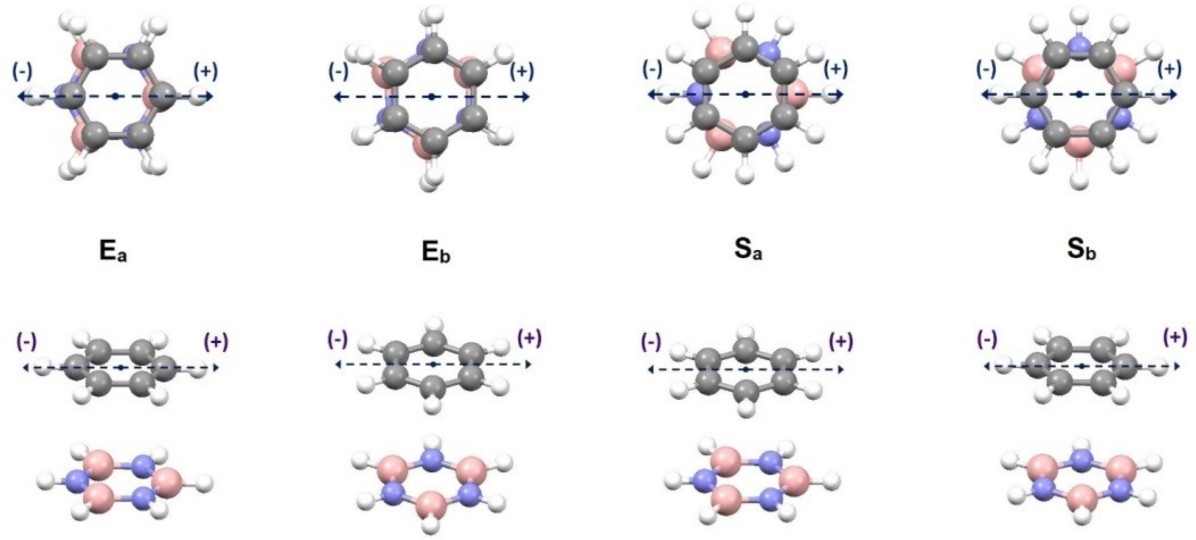

Figure S2. Top and side view of the model systems for the calculations of potential energy surfaces for borazine-benzene stacking. Benzene molecule was displaced in the directions denoted by arrows

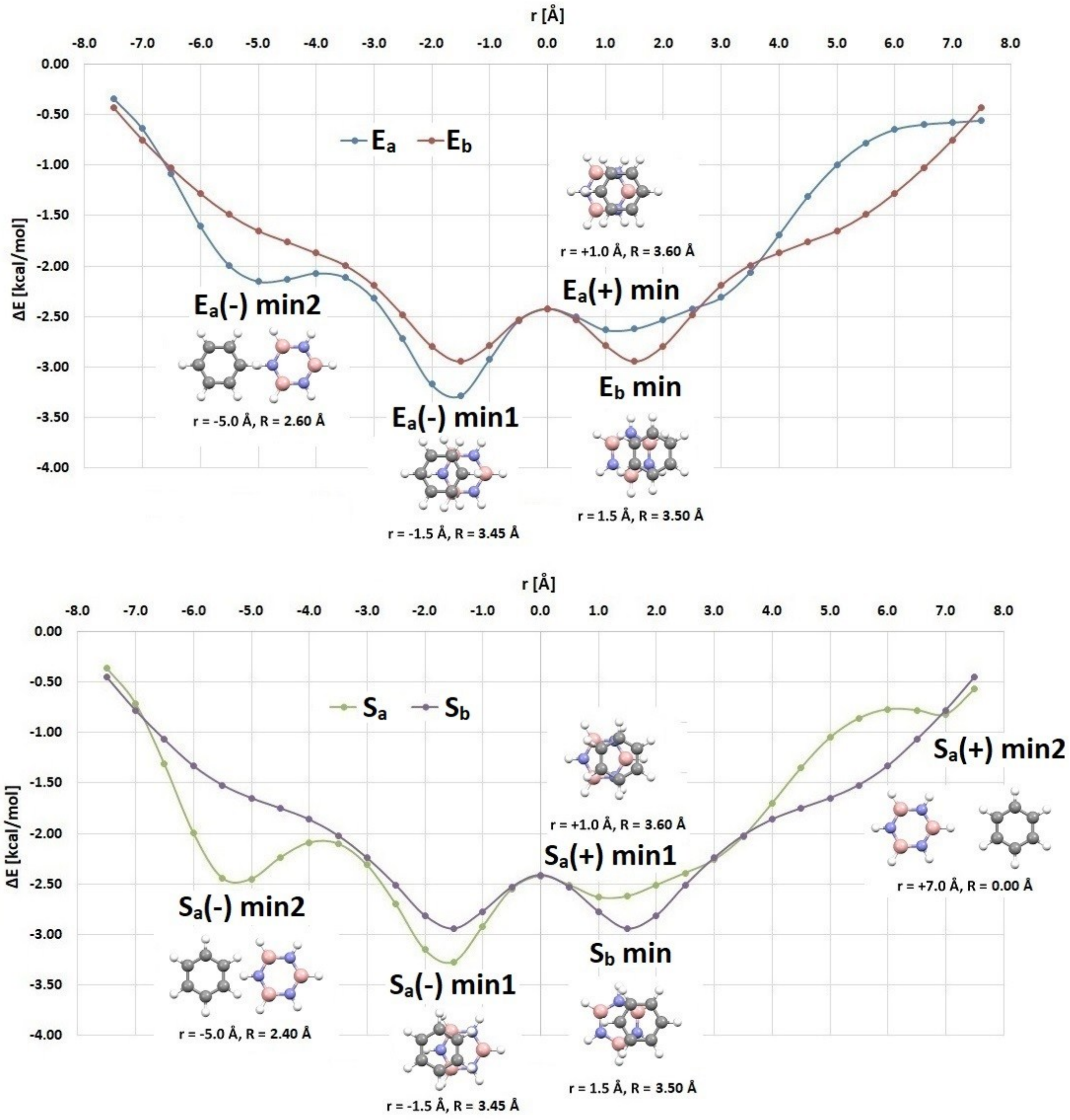

Figure S3. Potential energy curves for four model systems (Figure S2) for borazine-benzene stacking. The curves were calculated at B3LYP-D3/def2-TZVP level by changing the normal distances (R) for the series of offset (r) values, and they show the energies of the strongest interaction for each offset value. The top views of the geometries of the curve minima and their geometrical parameters are given. Negative and positive offsets are equivalent for curves E$_b$ and S$_b$, and the offsets for their minima are reported without signs.

INTERACTION ENERGIES FOR BORAZINE-BORAZINE POTENTIAL CURVE MINIMA IN DIFFERENT SOLVENTS

Table S2. B3LYP-D3/def2-TZVP interaction energies (in kcal/mol) for the minima on borazine-benzene potential energy curves (Figure S5) calculated in gas phase, and solvents of various polarity (methanol ε = 32.61, acetone ε = 20.49; cyclohexane ε = 2.02).

	gas	acetone	cyclohexane	methanol
parallel-displaced minima				
Ea(-) min1	-3.28	-3.11	-3.21	-3.11
Ea(+) min	-2.63	-2.58	-2.59	-2.58
Eb min	-2.94	-2.82	-2.87	-2.82
Sa(-) min1	-3.27	-3.10	-3.19	-3.09
Sa(+) min1	-2.63	-2.58	-2.58	-2.58
Sb min	-2.94	-2.82	-2.87	-2.82
minima with large offsets				
Ea(-) min2	-2.15	-1.65	-2.00	-1.63
Sa(-) min2	-2.45	-1.94	-2.29	-1.92
minimum with dihydrogen bond				
Sa(+) min2	-0.82	-0.86	-0.81	-0.86

GIBBS FREE ENERGIES OF FORMATION FOR OPTIMIZED BORAZINE-BENZENE DIMERS

Table S3. Gibbs free energies of formation (in kcal/mol) at 298 K of optimized borazine-benzene dimers at B3LYP-D3/def2TZVP level

structure	ΔG (kcal/mol)
E_a(-) min1 opt	4.37
S_a(-) min1 opt E_b min opt S_b min opt	3.01
S_a(+) min1 opt	6.02
E_a(+) min opt	4.92
E_a(-) min2 opt S_a(-) min2 opt	2.80
S_a(+) min2 opt	4.67

BORAZINE-BORAZINE STACKING – MODEL-SYSTEMS AND POTENTIAL ENERGY CURVES

Five model systems were considered for the calculations of borazine-borazine stacking potential energy surfaces (Figure S4). In the first model system, the orientation of borazine molecules is *antiparallel*, sandwich geometry is *eclipsed*, and one borazine was displaced *along* the direction of N-H (or B-H) bond (mode system **ap-E$_a$**). In the second model system, the orientation of borazines is *parallel*, sandwich geometry is *eclipsed*, and one borazine was displaced *along* the direction of N-H (or B-H) bond (model system **p-E$_a$**). In the third model system, the orientation of borazines is *antiparallel*, sandwich geometry is *eclipsed*, and one borazine was displaced in the direction between B-N bonds (model system **ap-E$_b$**). In the fourth model system, the orientation of borazines is *parallel*, sandwich geometry is *eclipsed*, and one borazine was displaced in the direction between B-N bonds (model system **p-E$_b$**). The fifth model system has *staggered* sandwich orientation (model system **S**); the displacements along the direction of N-H (or B-H) bond and in the direction between B-N bonds are equivalent.

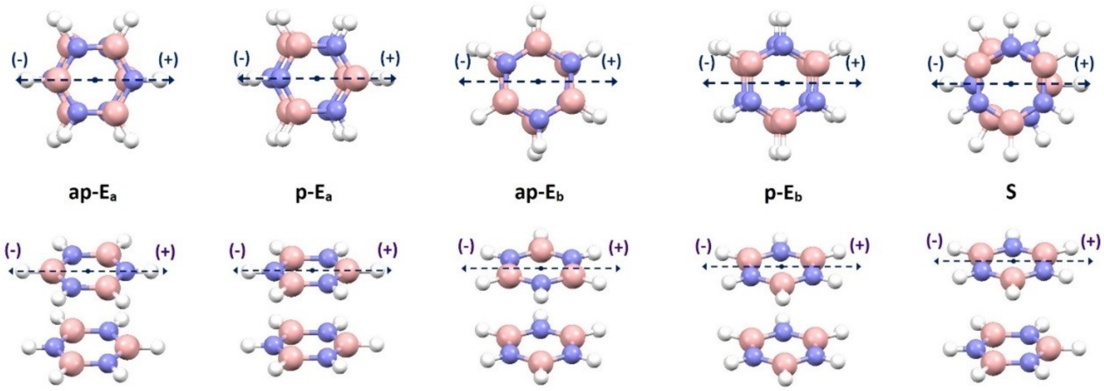

Figure S4. Model systems for the calculations of potential energy surfaces for borazine-borazine stacking. Upper borazine molecule was displaced in the directions denoted by arrows.

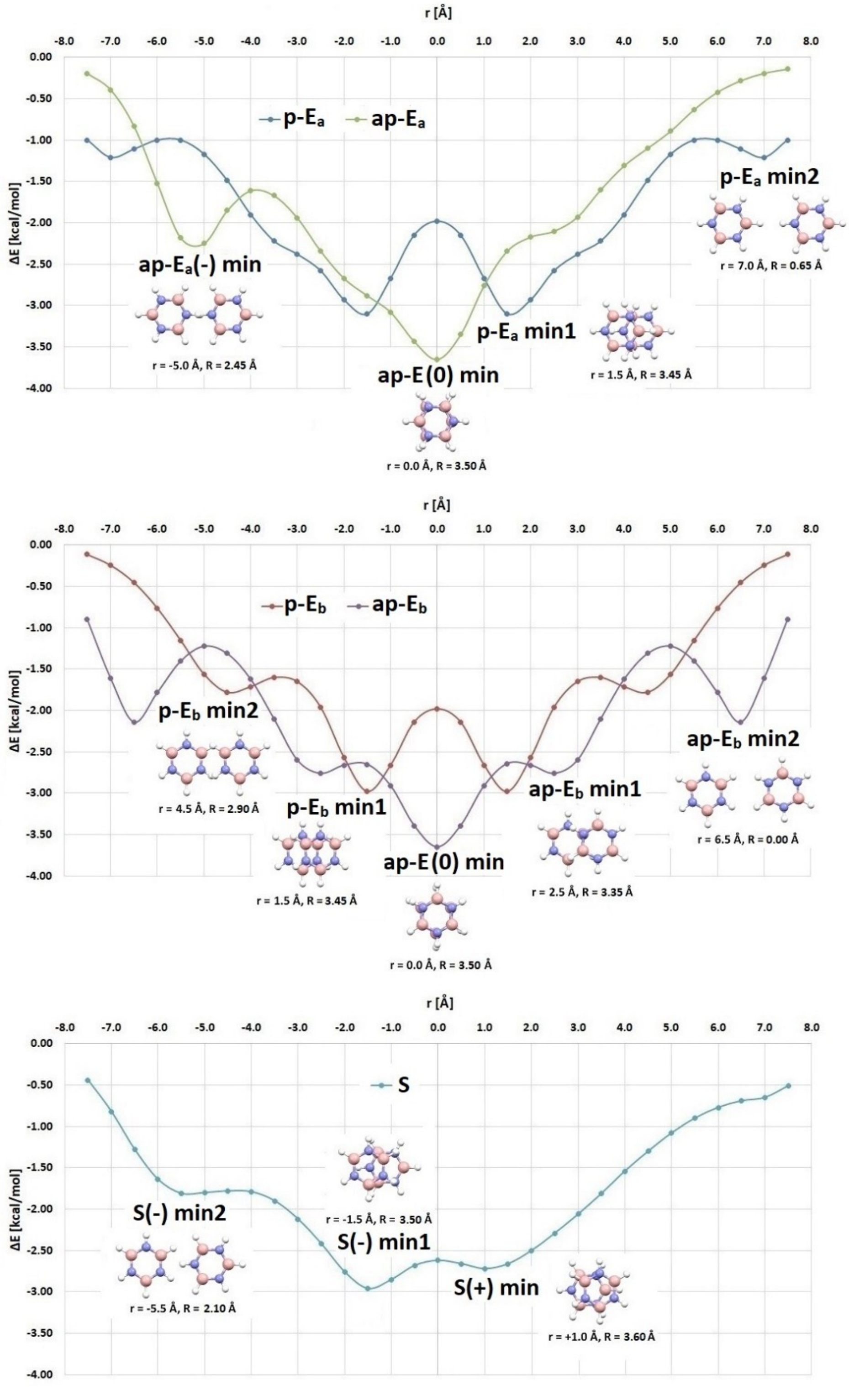

Figure S5. Potential energy curves for five model systems (Figure S4) for borazine-borazine stacking. The curves were calculated at B3LYP-D3/def2-TZVP level by changing the normal distances (R) for the series of offset values (r), and they show the energies of the strongest interaction for each offset value. The top views of the geometries of the curve minima and their geometrical parameters are given. Negative and positive offsets are equivalent for curves **p-E_a, ap-E_b** and **p-E_b**, and the offsets for their minima are reported without signs.

INTERACTION ENERGIES FOR BORAZINE-BORAZINE POTENTIAL CURVE MINIMA IN DIFFERENT SOLVENTS

Table S4. B3LYP-D3/def2-TZVP interaction energies (in kcal/mol) for the minima on borazine-borazine potential energy curves (Figure S5) calculated in gas phase, and solvents of various polarity (methanol ε = 32.61, acetone ε = 20.49; cyclohexane ε = 2.02).

	gas	acetone	cyclohexane	methanol
sandwich minimum				
ap-E(0) min	-3.65	-3.37	-3.53	-3.36
parallel-displaced minima				
p-E_a min1	-3.10	-3.06	-3.07	-3.06
ap-E_b min1	-2.76	-2.58	-2.69	-2.58
p-E_b min1	-2.98	-2.96	-2.96	-2.96
S(-) min1	-2.96	-2.84	-2.90	-2.84
S(+) min	-2.72	-2.67	-2.69	-2.67
minima with large offsets				
ap-E_a(-) min	-2.25	-1.98	-2.17	-1.97
p-E_b min2	-1.78	-1.55	-1.70	-1.54
S(-) min2	-1.81	-1.53	-1.72	-1.52
minima with dihydrogen bonding				
p-E_a min2	-1.21	-0.99	-1.13	-0.98
ap-E_b min2	-2.14	-1.74	-1.98	-1.73

GIBBS FREE ENERGIES OF FORMATION FOR OPTIMIZED BORAZINE-BORAZINE DIMERS

Table S5. Gibbs free energies of formation (in kcal/mol) at 298 K of optimized borazine-borazine dimers at B3LYP-D3/def2TZVP level

	ΔG
ap-E(0) min opt S(+) min opt	5.11
p-E_a min1 opt S(-) min1 opt	3.26
p-E_b min2 opt	3.52
ap-E_b min1 opt	3.34
ap-E_a(-) min opt	4.76
p-E_b min1 opt	4.12
ap-E_b min2 opt	5.83
p-E_a min2 opt	3.84
S(-) min2 opt	2.93

INTERACTIONS IN CRYSTAL STRUCTURES OF BORAZINE-RELATED COMPOUNDS

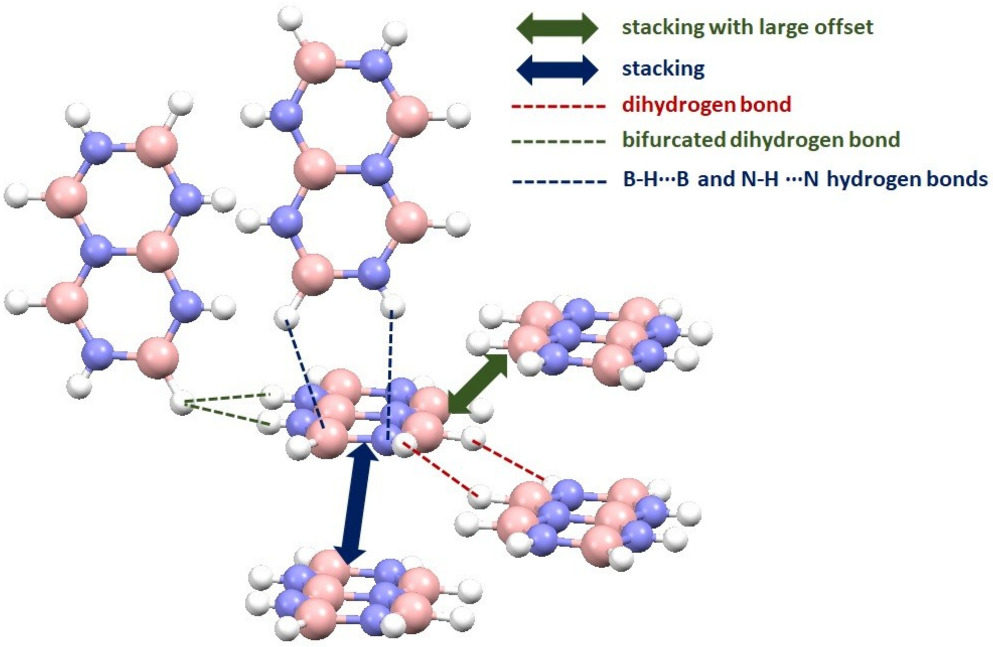

Figure S6. Interactions in crystal structure of $B_5N_5H_8$, pentaazapentaboranaphthalene (CSD refcode ZUWVIW)

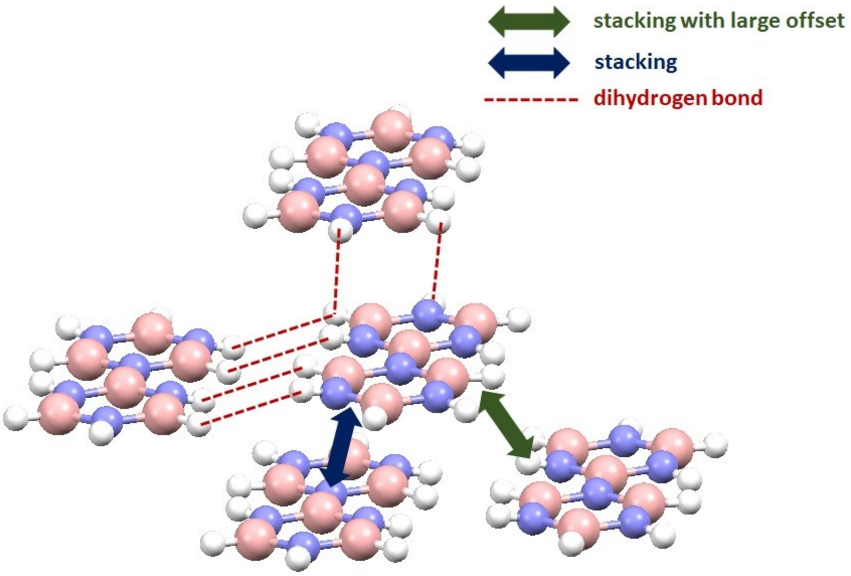

Figure S7. Interactions in crystal structure of $B_6N_6H_{10}$, 1,2’-biborazine (CSD refcode ZUWVOC)

ELECTROSTATIC POTENTIAL MAPS FOR BORAZINE-RELATED COMPOUNDS

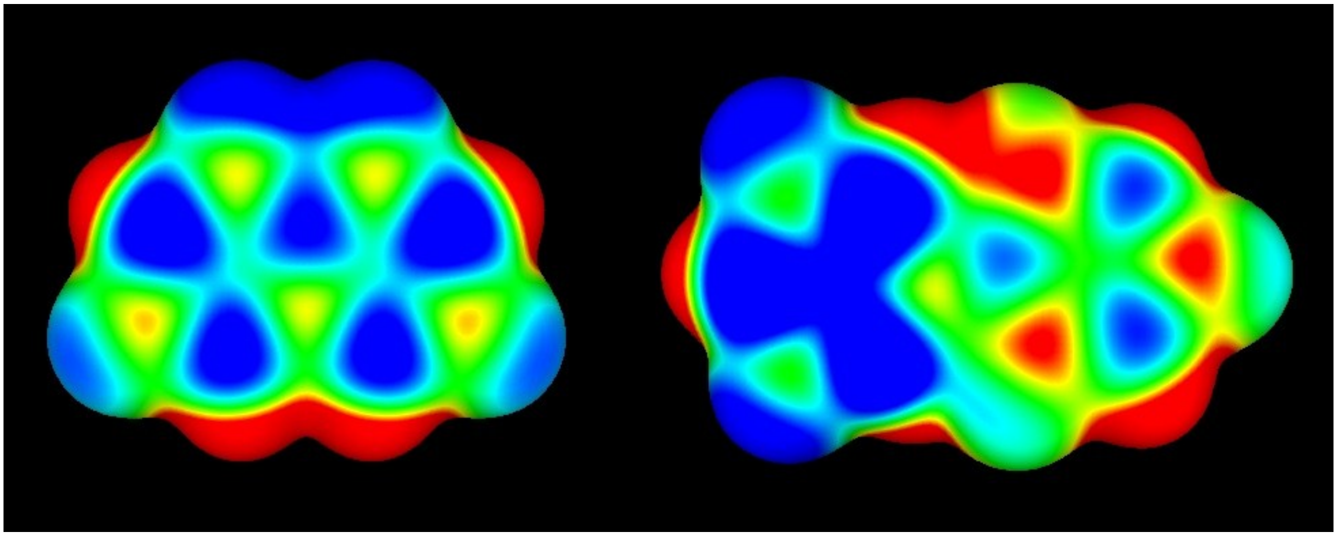

Figure S8. Electrostatic potentials of $B_5N_5H_8$ (left) and $B_6N_6H_{10}$ (right) plotted at the outer contour of 0.001 a.u. The maps were obtained from Gaussian wave functions calculated at B3LYP-D3/def2-TZVP level of theory. The color scale is: red > 6.3 kcal/mol, yellow 0.0 – 6.3 kcal/mol, green -6.3 – 0.0 kcal/mol, blue < -6.3 kcal/mol.