Supporting Information

STACKING INTERACTIONS OF RESONANCE-ASSISTED HYDROGEN-BRIDGED RINGS

AND C_6-AROMATIC RINGS

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Geometric parameters of six-membered RAHB/C_6-aromatic contacts found in CSD (Cambridge Structural Database), for HNNCCO, HOCCCO and HNCCCO RAHB ring atom sequences

The distribution of dihedral angles between RAHB ring and C_6-aromatic ring in their mutual contacts (Figure S1) and a scatterplot indicating the relation between interplane separations and horizontal displacements of parallel contacts (Figure S2) are shown for HNNCCO, HOCCCO and HNCCCO RAHB ring atom sequences. Contacts of all three groups are mostly parallel stacked, as in the whole set of RAHB/C_6-aromatic contacts. (Figures 3 and 4). It can be noticed that the tendency of forming parallel contacts with C_6-aromatic rings is more pronounced in the group of HNNCCO RAHB ring atom sequences than in the other two groups (Figure S1).
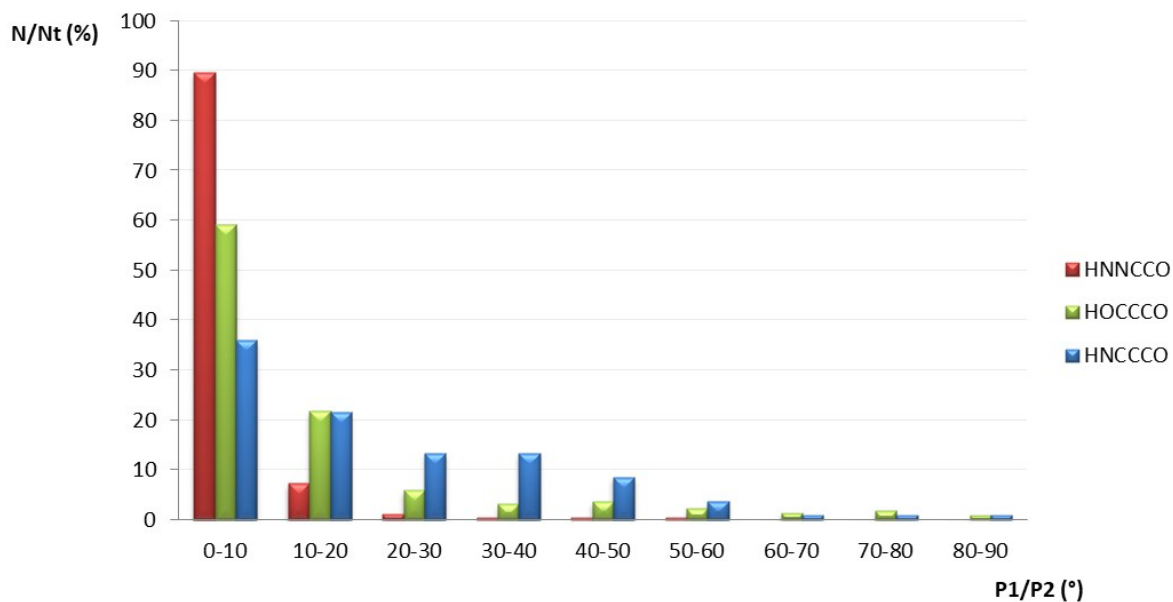
Figure S1. Distributions of dihedral angles between RAHB and C_6-aromatic rings for every group of RAHB ring atom sequences found in CSD. The distributions are displayed as percentages of the number of contacts of a particular group in a particular range of dihedral angle values (N) from the total number of contacts of a particular group (Nt).
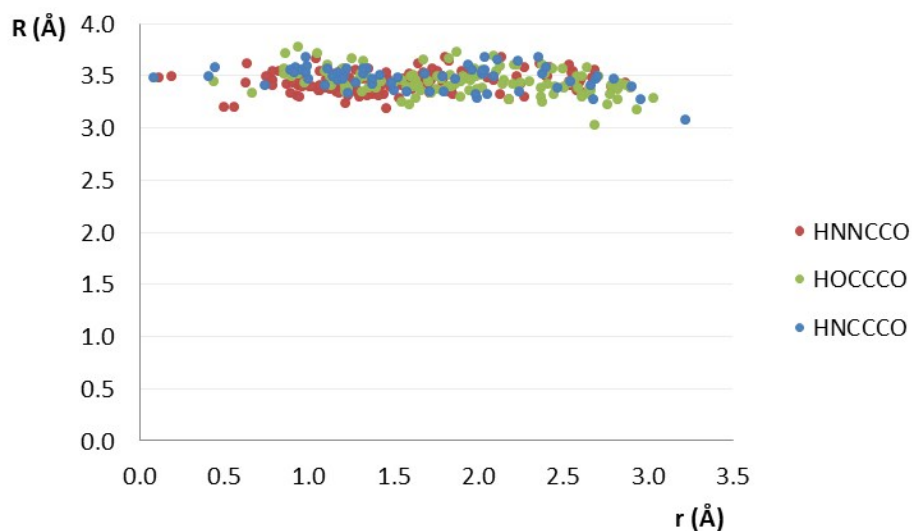
Figure S2. A scatterplot showing the relation between interplane separations and horizontal displacements of parallel RAHB/C_6-aromatic ring contacts found in the CSD of the three groups of RAHB ring atom sequences

Effect of RAHB ring substituents on RAHB/C_6-aromatic contacts

It is observed that there is a relatively large number of RAHB/C_6-aromatic contacts in CSD where a RAHB ring is substituted by a C_6-aromatic group (346 contacts, from totally 698 RAHB/C_6-aromatic contacts, CSD Version 5.40, updates Feb.2019). There is a slightly higher tendency for stacking between RAHB rings, substituted by a C_6-aromatic group (where at least one C_6-aromatic substituent is on either D, Z, Y, X or A position, Figure 2a) and C_6-aromatic rings, since 65% of these contacts are parallel (224 from totally 346 contacts, CSD Version 5.40, updates Feb.2019), comparing with 59% of parallel contacts in the total set of RAHB/C_6-aromatic contacts (413 parallel contacts, from totally 698 contacts, CSD Version 5.40, updates Feb.2019).

Evaluation of methods for the interaction energy calculations

The methods for the interaction energy calculations were chosen based on agreement with CCSD(T)/CBS (Complete Basis Set) method at certain points of potential energy surface. The method that shows good results at three points along the same direction is used for calculating the potential energy curve along that direction (Figure S3). The results are shown in Tables S1-S5. All potential energy curves are calculated at MP2/cc-pVTZ level, since this method is in good agreement with CCSD(T)/CBS method.
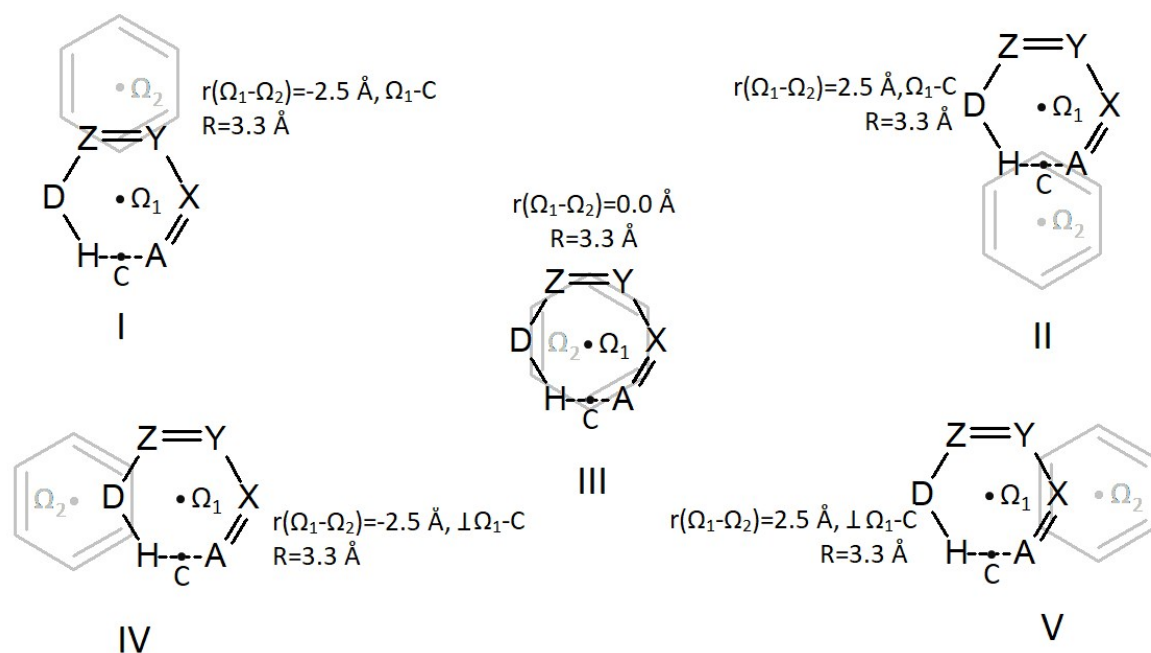

Figure S3. The selected points on the potential energy surface (I-V, with geometrical parameters-Figure 2a), that were used for the evaluation of methods for the calculation of interaction energies

Table S1. Interaction energies calculated at various levels of theory and relative errors (with respect to CCSD(T)/CBS method) of RAHB/benzene systems of the geometry I (Figure S3)

	INTERACTION ENERGIES (kcal/mol)				RELATIVE ERRORS (%)			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
$H_4C_3O_2$/benzene								
MP2	-0.92	-2.5	-2.90	-1.5	63.64	1.19	14.65	40.71
TPSS-D3	-2.31	-2.38	-2.57	-2.54	8.70	5.93	1.58	0.40
BLYP-D3	-2.18	-2.45	-2.42	-2.42	13.83	3.16	4.35	4.35
BP86-D3	-2.55	-2.78	-2.9	-2.84	0.79	9.88	14.62	12.25
PBE1PBE-D3	-2.24	-2.37	-2.55	-2.53	11.46	6.32	0.79	0.00
M05-D3	-2.05	-2.07	-2.5	-2.48	18.97	18.18	1.19	1.98
M06-D3	-2.7	-2.89	-3.49	-3.41	6.72	14.23	37.94	34.78
M052X-D3	-2.1	-2.44	-2.68	-2.62	17.00	3.56	5.93	3.56
M06HF-D3	-2.74	-2.63	-3.43	-3.35	8.30	3.95	35.57	32.41
CCSD(T)/CBS	-2.53							
H_5C_3NO/benzene								
MP2	-0.5	-2.23	-2.70	-1.15	77.88	1.33	19.47	49.12
TPSS-D3	-1.93	-2.04	-2.25	-2.18	14.60	9.73	0.44	3.54
BLYP-D3	-1.81	-2.11	-2.11	-2.06	19.91	6.64	6.64	8.85
BP86-D3	-2.22	-2.51	-2.66	-2.55	1.77	11.06	17.70	12.83
PBE1PBE-D3	-1.81	-1.98	-2.2	-2.14	19.91	12.39	2.65	5.31
M05-D3	-1.66	-1.71	-2.18	-2.12	26.55	24.34	3.54	6.19
M06-D3	-2.46	-2.72	-3.44	-3.29	8.85	20.35	52.21	45.58
M052X-D3	-1.68	-2.07	-2.38	-2.3	25.66	8.41	5.31	1.77
M06HF-D3	-2.31	-2.26	-3.14	-3.06	2.21	0.00	38.94	35.40
CCSD(T)/CBS	-2.26							
$H_4C_2N_2O$/benzene								
MP2	-0.72	-1.52	-1.87	-1.2	54.72	4.40	17.61	24.53
TPSS-D3	-1.47	-1.61	-1.67	-1.62	7.55	1.26	5.03	1.89
BLYP-D3	-1.23	-1.31	-1.29	-1.27	22.64	17.61	18.87	20.13
BP86-D3	-1.08	-1.26	-1.27	-1.2	32.08	20.75	20.13	24.53
PBE1PBE-D3	-1.37	-1.56	-1.64	-1.58	13.84	1.89	3.14	0.63
M05-D3	-1.46	-1.61	-1.88	-1.8	8.18	1.26	18.24	13.21
M06-D3	-1.73	-1.87	-2.22	-2.04	8.81	17.61	39.62	28.30
M052X-D3	-1.26	-1.6	-1.74	-1.64	20.75	0.63	9.43	3.14
M06HF-D3	-1.26	-1.39	-1.72	-1.61	20.75	12.58	8.18	1.26
CCSD(T)/CBS	-1.59							

Table S2. Interaction energies calculated at various levels of theory and relative errors (with respect to CCSD(T)/CBS method) of RAHB/benzene systems of the geometry II (Figure S3)

	INTERACTION ENERGIES (kcal/mol)				RELATIVE ERRORS (%)			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
	$H_4C_3O_2$/benzene							
MP2	-0.35	-1.37	-1.75	-0.73	76.35	7.43	18.01	50.68
TPSS-D3	-1.36	-1.41	-1.46	-1.33	8.11	4.73	1.35	10.14
BLYP-D3	-1.44	-1.43	-1.41	-1.3	2.70	3.38	4.73	12.16
BP86-D3	-1.2	-1.36	-1.39	-1.22	18.92	8.11	6.08	17.57
PBE1PBE-D3	-1.13	-1.26	-1.33	-1.2	23.65	14.86	10.14	18.92
M05-D3	-1.35	-1.4	-1.63	-1.51	8.78	5.41	10.14	2.03
M06-D3	-1.49	-1.67	-1.91	-1.78	0.68	12.84	29.05	20.27
M052X-D3	-0.91	-1.18	-1.31	-1.17	38.51	20.27	11.49	20.95
M06HF-D3	-0.88	-0.84	-1.28	-1.16	40.54	43.24	13.51	21.62
CCSD(T)/CBS	**-1.48**							
	H_5C_3NO/benzene							
MP2	-0.14	-1.26	-1.69	-0.56	90.00	10.00	20.71	60.00
TPSS-D3	-1.24	-1.33	-1.4	-1.22	11.43	5.00	0.00	12.86
BLYP-D3	-1.3	-1.33	-1.33	-1.16	7.14	5.00	5.00	17.14
BP86-D3	-1.11	-1.32	-1.38	-1.15	20.71	5.71	1.43	17.86
PBE1PBE-D3	-0.98	-1.16	-1.26	-1.08	30.00	17.14	10.00	22.86
M05-D3	-1.25	-1.31	-1.59	-1.43	10.71	6.43	13.57	2.14
M06-D3	-1.33	-1.58	-1.95	-1.77	5.00	12.86	39.29	26.43
M052X-D3	-0.76	-1.08	-1.27	-1.09	45.71	22.86	9.29	22.14
M06HF-D3	-0.59	-0.62	-1.13	-1	57.86	55.71	19.29	28.57
CCSD(T)/CBS	**-1.40**							
	$H_4C_2N_2O$/benzene							
MP2	-0.64	-1.11	-1.38	-0.88	43.36	1.77	22.12	22.12
TPSS-D3	-1.25	-1.25	-1.29	-1.25	10.62	10.62	14.16	10.62
BLYP-D3	-1	-0.89	-0.88	-0.83	11.50	21.24	22.12	26.55
BP86-D3	-0.72	-0.75	-0.76	-0.68	36.28	33.63	32.74	39.82
PBE1PBE-D3	-1.09	-1.16	-1.21	-1.15	3.54	2.65	7.08	1.77
M05-D3	-1.05	-1.22	-1.35	-1.27	7.08	7.96	19.47	12.39
M06-D3	-1.23	-1.31	-1.4	-1.28	8.85	15.93	23.89	13.27
M052X-D3	-0.89	-1.11	-1.2	-1.12	21.24	1.77	6.19	0.88
M06HF-D3	-0.74	-0.79	-0.95	-0.89	34.51	30.09	15.93	21.24
CCSD(T)/CBS	**-1.13**							

Table S3. Interaction energies calculated at various levels of theory and relative errors (with respect to CCSD(T)/CBS method) of RAHB/benzene systems of the geometry III (Figure S3)

	INTERACTION ENERGIES (kcal/mol)				RELATIVE ERRORS (%)			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
$H_4C_3O_2$/benzene								
MP2	0.43	-1.58	-2.02	0.01	127.92	2.60	30.88	100.65
TPSS-D3	-1.16	-1.05	-1.22	-1.09	24.68	31.82	20.78	29.22
BLYP-D3	-1.31	-1.42	-1.32	-1.25	14.94	7.79	14.29	18.83
BP86-D3	-1.81	-1.98	-2.05	-1.87	17.53	28.57	33.12	21.43
PBE1PBE-D3	-0.91	-0.9	-1.04	-0.93	40.91	41.56	32.47	39.61
M05-D3	-0.84	-0.64	-1.08	-0.97	45.45	58.44	29.87	37.01
M06-D3	-1.59	-1.77	-2.16	-2.04	3.25	14.94	40.26	32.47
M052X-D3	-0.68	-0.94	-1.13	-1	55.84	38.96	26.62	35.06
M06HF-D3	-1.46	-0.95	-1.92	-1.78	5.19	38.31	24.68	15.58
CCSD(T)/CBS	**-1.54**							
H_5C_3NO/benzene								
MP2	1.58	-0.64	-1.13	1.16	367.80	8.47	91.53	296.61
TPSS-D3	-0.21	-0.13	-0.35	-0.12	64.41	77.97	40.68	79.66
BLYP-D3	-0.31	-0.5	-0.41	-0.22	47.46	15.25	30.51	62.71
BP86-D3	-0.96	-1.18	-1.31	-1	62.71	100.00	122.03	69.49
PBE1PBE-D3	0.19	0.14	-0.05	0.17	132.20	123.73	91.53	128.81
M05-D3	0.29	0.43	-0.05	0.2	149.15	172.88	91.53	133.90
M06-D3	-0.68	-0.96	-1.51	-1.21	15.25	62.71	155.93	105.08
M052X-D3	0.53	0.22	-0.07	0.14	189.83	137.29	88.14	123.73
M06HF-D3	-0.2	0.26	-0.84	-0.7	66.10	144.07	42.37	18.64
CCSD(T)/CBS	**-0.59**							
$H_4C_2N_2O$/benzene								
MP2	0.37	-1.73	-2.21	-0.13	124.18	13.07	44.44	91.50
TPSS-D3	-1.05	-0.95	-1.13	-1.01	31.37	37.91	26.14	33.99

BLYP-D3	-1.26	-1.4	-1.26	-1.17	17.65	8.50	17.65	23.53
BP86-D3	-1.75	-1.95	-2.02	-1.84	14.38	27.45	32.03	20.26
PBE1PBE-D3	-0.74	-0.76	-0.91	-0.81	51.63	50.33	40.52	47.06
M05-D3	-0.76	-0.57	-1.04	-0.92	50.33	62.75	32.03	39.87
M06-D3	-1.54	-1.64	-2.19	-2.06	0.65	7.19	43.14	34.64
M052X-D3	-0.47	-0.71	-1	-0.88	69.28	53.59	34.64	42.48
M06HF-D3	-1.18	-0.6	-1.68	-1.66	22.88	60.78	9.80	8.50
CCSD(T)/CBS	**-1.53**							

Table S4. Interaction energies calculated at various levels of theory and relative errors (with respect to CCSD(T)/CBS method) of RAHB/benzene systems of the geometry IV (Figure S3)

	INTERACTION ENERGIES (kcal/mol)				RELATIVE ERRORS (%)			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
	$H_4C_3O_2$/benzene							
MP2	-0.51	-1.72	-2.11	-0.95	73.30	9.95	10.36	50.26
TPSS-D3	-1.83	-1.91	-1.98	-1.87	4.19	0.00	3.66	2.09
BLYP-D3	-1.88	-1.97	-1.94	-1.84	1.57	3.14	1.57	3.66
BP86-D3	-1.76	-2	-2.02	-1.86	7.85	4.71	5.76	2.62
PBE1PBE-D3	-1.69	-1.86	-1.93	-1.82	11.52	2.62	1.05	4.71
M05-D3	-1.86	-1.93	-2.18	-2.1	2.62	1.05	14.14	9.95
M06-D3	-2.13	-2.37	-2.66	-2.56	11.52	24.08	39.27	34.03
M052X-D3	-1.54	-1.87	-2.01	-1.87	19.37	2.09	5.24	2.09
M06HF-D3	-1.67	-1.69	-2.14	-2.01	12.57	11.52	12.04	5.24
CCSD(T)/CBS	**-1.91**							
	H_5C_3NO/benzene							
MP2	-1.55	-3.02	-3.44	-2.06	50.32	3.21	10.26	33.97
TPSS-D3	-3.13	-3.18	-3.29	-3.27	0.32	1.92	5.45	4.81
BLYP-D3	-3.04	-3.21	-3.1	-3.1	2.56	2.88	0.64	0.64
BP86-D3	-3.24	-3.47	-3.53	-3.47	3.85	11.22	13.14	11.22
PBE1PBE-D3	-3.06	-3.19	-3.31	-3.29	1.92	2.24	6.09	5.45
M05-D3	-3.01	-3.02	-3.33	-3.34	3.53	3.21	6.73	7.05
M06-D3	-3.55	-3.71	-4.27	-4.19	13.78	18.91	36.86	34.29
M052X-D3	-2.99	-3.27	-3.52	-3.46	4.17	4.81	12.82	10.90
M06HF-D3	-3.44	-3.36	-4.08	-4.06	10.26	7.69	30.77	30.13
CCSD(T)/CBS	**-3.12**							
	$H_4C_2N_2O$/benzene							
MP2	-1.4	-2.77	-3.20	-1.93	50.18	1.42	13.88	31.32
TPSS-D3	-2.89	-2.93	-3.03	-3.01	2.85	4.27	7.83	7.12
BLYP-D3	-2.87	-2.98	-2.86	-2.86	2.14	6.05	1.78	1.78
BP86-D3	-2.91	-3.13	-3.16	-3.11	3.56	11.39	12.46	10.68
PBE1PBE-D3	-2.75	-2.87	-2.98	-2.96	2.14	2.14	6.05	5.34
M05-D3	-2.78	-2.76	-3.07	-3.08	1.07	1.78	9.25	9.61
M06-D3	-3.23	-3.33	-3.82	-3.8	14.95	18.51	35.94	35.23

M052X-D3	-2.65	-2.92	-3.15	-3.1	5.69	3.91	12.10	10.32
M06HF-D3	-3.03	-2.93	-3.62	-3.62	7.83	4.27	28.83	28.83
CCSD(T)/CBS	**-2.81**							

Table S5. Interaction energies calculated at various levels of theory and relative errors (with respect to CCSD(T)/CBS method) of RAHB/benzene systems of the geometry V (Figure S3)

	INTERACTION ENERGIES (kcal/mol)				RELATIVE ERRORS (%)			
	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	6-31++G**
	$H_4C_3O_2$/benzene							
MP2	-1.25	-2.74	-3.11	-1.73	56.45	4.53	8.47	39.72
TPSS-D3	-2.46	-2.48	-2.62	-2.57	14.29	13.59	8.71	10.45
BLYP-D3	-2.39	-2.55	-2.49	-2.48	16.72	11.15	13.24	13.59
BP86-D3	-2.67	-2.85	-2.91	-2.83	6.97	0.70	1.39	1.39
PBE1PBE-D3	-2.46	-2.54	-2.68	-2.63	14.29	11.50	6.62	8.36
M05-D3	-2.38	-2.36	-2.72	-2.68	17.07	17.77	5.23	6.62
M06-D3	-2.9	-2.97	-3.49	-3.38	1.05	3.48	21.60	17.77
M052X-D3	-2.48	-2.73	-2.94	-2.85	13.59	4.88	2.44	0.70
M06HF-D3	-3.05	-2.86	-3.6	-3.5	6.27	0.35	25.44	21.95
CCSD(T)/CBS	**-2.87**							
	H_5C_3NO/benzene							
MP2	-0.56	-2.13	-2.58	-1.1	75.22	5.75	14.16	51.33
TPSS-D3	-1.77	-1.8	-1.98	-1.87	21.68	20.35	12.39	17.26
BLYP-D3	-1.74	-1.89	-1.88	-1.8	23.01	16.37	16.81	20.35
BP86-D3	-1.99	-2.2	-2.31	-2.15	11.95	2.65	2.21	4.87
PBE1PBE-D3	-1.69	-1.8	-1.97	-1.86	25.22	20.35	12.83	17.70
M05-D3	-1.7	-1.7	-2.1	-2	24.78	24.78	7.08	11.50
M06-D3	-2.33	-2.48	-3.06	-2.89	3.10	9.73	35.40	27.88
M052X-D3	-1.67	-1.98	-2.23	-2.1	26.11	12.39	1.33	7.08
M06HF-D3	-2.15	-2.02	-2.78	-2.66	4.87	10.62	23.01	17.70
CCSD(T)/CBS	**-2.26**							
	$H_4C_2N_2O$/benzene							
MP2	-1.53	-3.04	-3.48	-2.12	50.80	2.25	11.90	31.83
TPSS-D3	-2.55	-2.58	-2.74	-2.69	18.01	17.04	11.90	13.50
BLYP-D3	-2.50	-2.65	-2.62	-2.60	19.61	14.79	15.76	16.40
BP86-D3	-2.73	-2.92	-3.00	-2.92	12.22	6.11	3.54	6.11
PBE1PBE-D3	-2.59	-2.69	-2.85	-2.80	16.72	13.50	8.36	9.97
M05-D3	-2.62	-2.62	-3.03	-3.02	15.76	15.76	2.57	2.89
M06-D3	-3.12	-3.22	-3.81	-3.75	0.32	3.54	22.51	20.58

M052X-D3	-2.66	-2.98	-3.20	-3.12	14.47	4.18	2.89	0.32
M06HF-D3	-3.16	-3.10	-3.79	-3.73	1.61	0.32	21.86	19.94
CCSD(T)/CBS	**-3.11**							

Dependences of interplane distances on horizontal displacements
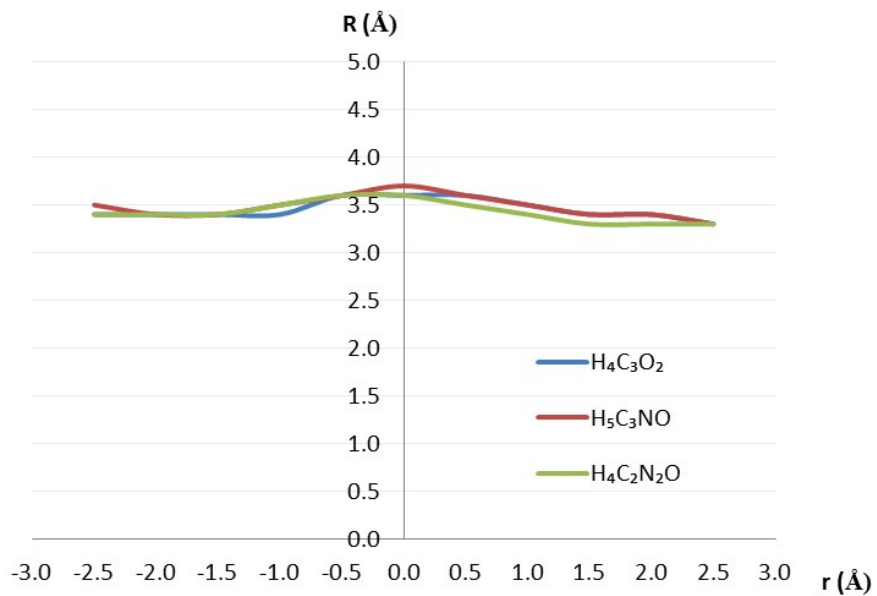
(a)
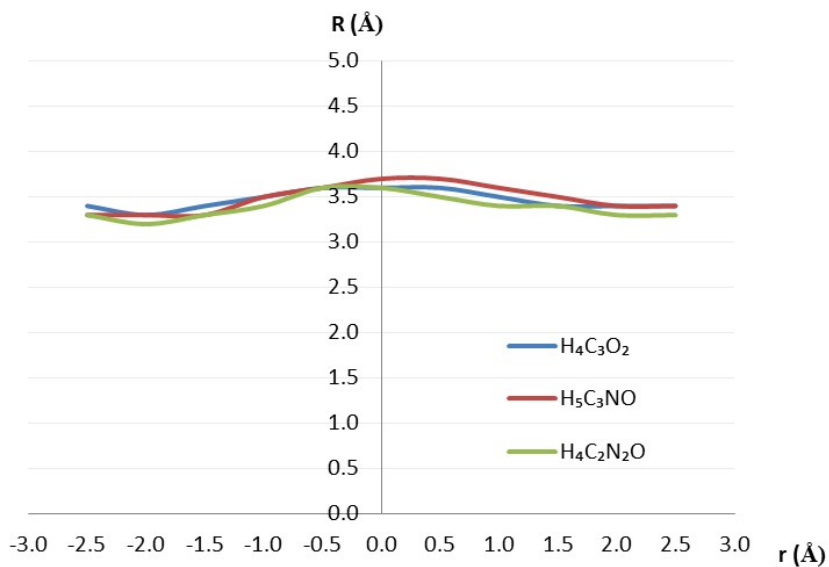
(b)

Figure S4. The calculated optimal distance dependences on horizontal displacements in parallel RAHB/C_6-aromatic ring systems a) along Ω_1-C direction; b) along the direction orthogonal to Ω_1-C in the RAHB ring plane (Figure 7)

The optimizations of the minima geometries

RAHB/benzene geometries are optimized at MP2/cc-pVTZ level by using the starting geometries that correspond to the potential curves minima (Figure 9). The geometries of the optimized systems and the interaction energies at CCSD(T)/CBS level are given in Figure S5 and Table S6, respectively. Two geometries are significantly more stable; the interaction energies are -4.42 kcal/mol, obtained by the optimization of H_5C_3NO/benzene minimum along the direction orthogonal to Ω_1-C (Figure 9b) and -4.15 kcal/mol obtained by optimization of $H_4C_2N_2O$/benzene minimum along the same direction (Figure 9b), but these optimized geometries do not correspond to parallel orientations of RAHB and benzene rings (Figure S5c), since dihedral angles (P1/P2) are larger than 10°. The most stable optimized stacking geometries are obtained by using $H_4C_3O_2$/benzene systems corresponding to the minima in both directions as starting geometries. These obtained optimized geometries are almost the same, with interaction energies of -3.73 kcal/mol (Table S6, Figure S5).

Table S6. Interaction energies (in kcal/mol) calculated at CCSD(T)/CBS level of optimized and non-optimized (corresponding to the potential curves minima, Figure 9) RAHB/benzene systems

	Optimized	Non-optimized
Direction Ω_1-C		
$H_4C_3O_2$/benzene	-3.73	-3.54
H_5C_3NO/benzene	-3.01	-2.94
$H_4C_2N_2O$/benzene	-3.48	-2.89
Direction orthogonal to Ω_1-C in the RAHB ring plane		
$H_4C_3O_2$/benzene	-3.73	-3.06
H_5C_3NO/benzene	-4.42	-3.47
$H_4C_2N_2O$/benzene	-4.15	-3.20

The shortening of the H-O hydrogen bonds, comparing with the monomer geometries, occurs in systems where stacked arrangement is preserved ($H_4C_3O_2$/benzene systems, Figures S5b and S5c,

as well as H_5C_3NO/benzene and $H_4C_2N_2O$/benzene systems, Figure S5b), while the H-O bonds become longer than in monomer geometries in optimized systems where stacked arrangement is not preserved (H_5C_3NO/benzene and $H_4C_2N_2O$/benzene, Figure S5c).

d(H-O) = 1.639 Å   d(H-O) = 1.898 Å   d(H-O) = 1.853 Å

a)

P1/P2 = 4.48°   P1/P2 = 5.26°   P1/P2 = 2.22°

d(H-O) = 1.631 Å   d(H-O) = 1.894 Å   d(H-O) = 1.851 Å

b)

P1/P2 = 4.51°   P1/P2 = 13.71°   P1/P2 = 14.08°

d(H-O) = 1.632 Å   d(H-O) = 1.909 Å   d(H-O) = 1.869 Å

c)
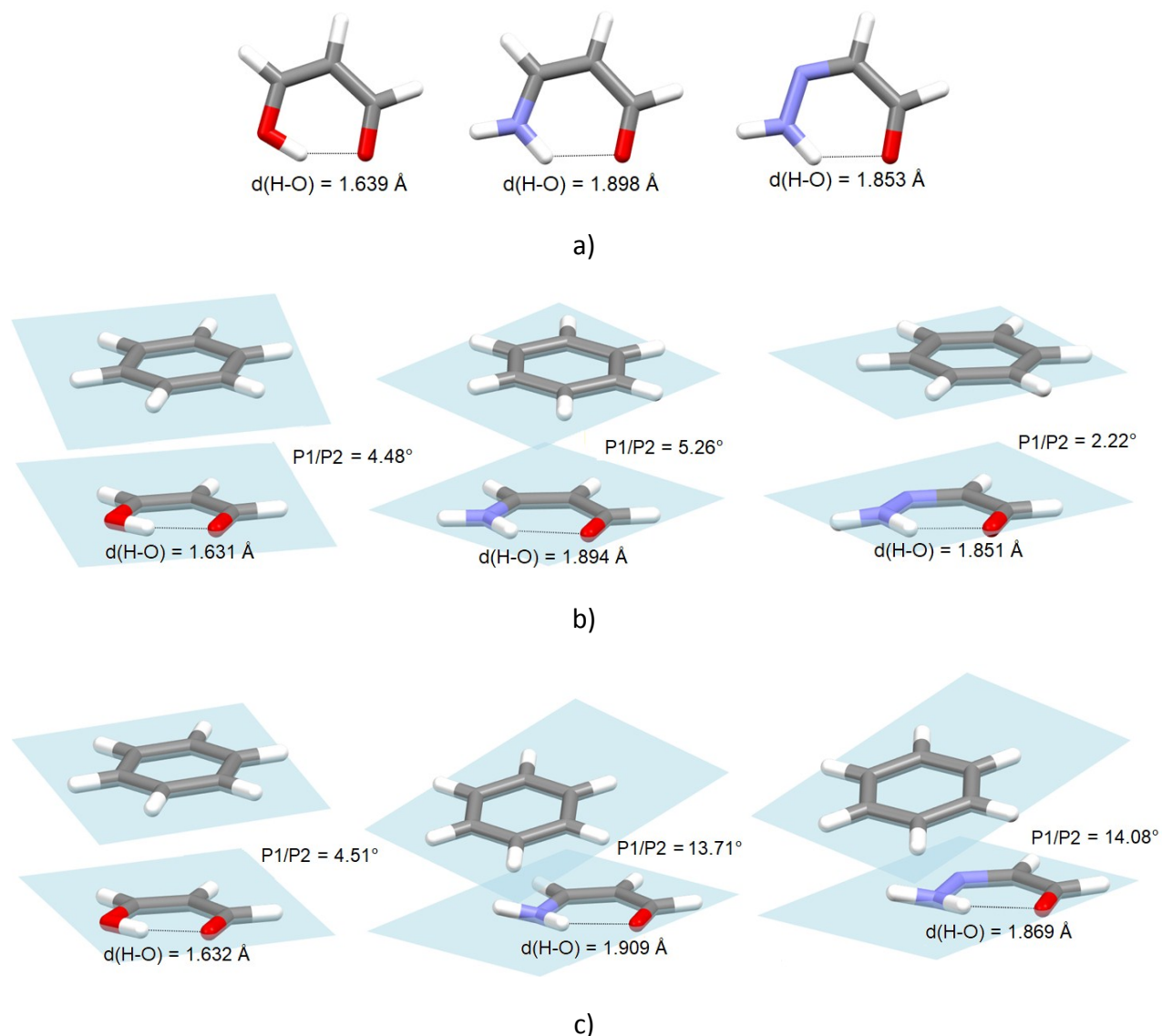
Figure S5. Optimized RAHB ring monomers and optimized RAHB/benzene systems with d(H-O) distances and angles between RAHB and benzene ring planes a) the optimized monomer geometries b) the optimized $H_4C_3O_2$/benzene, H_5C_3NO/benzene and $H_4C_2N_2O$/benzene systems, obtained by using potential curve minima along Ω_1-C direction as starting geometries; c)

optimized $H_4C_3O_2$/benzene, H_5C_3NO/benzene and $H_4C_2N_2O$/benzene systems, obtained by using potential curve minima along the direction orthogonal to Ω_1-C as starting geometries

Interaction energy calculations of the RAHB/C_6-aromatic contacts from the CSD

The model systems for the calculations were structures of stacked RAHB and C_6-aromatic rings, extracted from the CSD and modified, so that all substituents, present in either RAHB or C_6-aromatic ring, were replaced by hydrogen atoms (Figure S6), by keeping all valence and torsion angles unchanged, while setting bond lengths identical to those in the optimized RAHB molecules (at MP2/cc-pVTZ level). The interaction energies were calculated at MP2/cc-pVTZ level (Table S7), which is used for the calculation of the potential energy curves (Figure 8), since it is in good agreement with CCSD(T)/CBS method (Tables S1-S5).
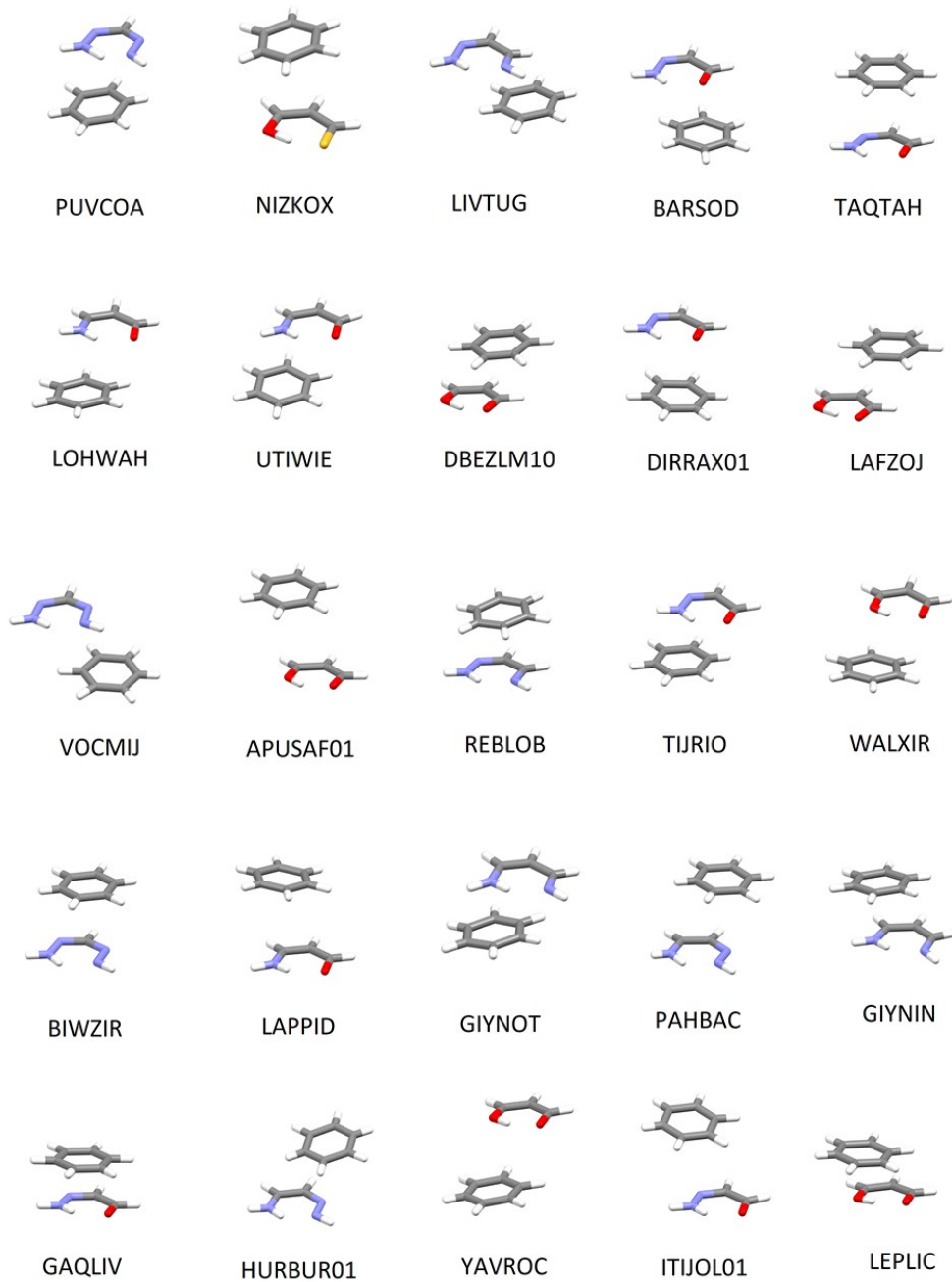
Figure S6. The model systems for the interaction energy calculations, obtained by replacing all ring substituents by hydrogen atoms. The refcodes of the original crystal structures are given.

Table S7. Interaction energies of the selected model systems (Figure S6), with original structure

refcodes and the system parameters as defined in Figure 2a

RAHB ring atom sequence (HDZYXA)	refcode	P1/P2 (°)	R (Å)	r (Å)	ΔE (kcal/mol)
HNNCNN	PUVCOA	3.8	3.3	1.1	-3.98
HOCCCS	NIZKOX	7.8	3.6	1.6	-3.98
HNNCCN	LIVTUG	3.3	3.3	2.5	-3.37
HNNCCO	BARSOD	2.7	3.3	1.3	-3.24
HNNCCO	TAQTAH	5.5	3.3	1.3	-3.18
HNCCCO	LOHWAH	6.6	3.5	1.4	-3.13
HNCCCO	UTIWIE	8.3	3.5	1.4	-2.96
HOCCCO	DBEZLM10	4.7	3.4	1.9	-2.94
HNNCCO	DIRRAX01	3.9	3.4	1.1	-2.79
HOCCCO	LAFZOJ	1.1	3.4	2.3	-2.71
HOCCCO	APUSAF01	6.1	3.6	2.6	-2.62
HNNCCN	REBLOB	5.8	3.5	0.6	-2.61
HNNCCO	TIJRIO	5.1	3.4	1.2	-2.58
HOCCCO	WALXIR	6.2	3.3	1.6	-2.56
HNNCNN	VOCMIJ	5.0	3.5	2.4	-2.55
HNNCNN	BIWZIR	4.5	3.4	1.0	-2.54
HNCCCO	LAPPID	6.3	3.5	2.4	-2.42
HNCCCN	GIYNOT	8.5	3.6	1.6	-2.34
HNCCNN	PAHBAC	3.5	3.5	1.8	-2.14
HNCCCN	GIYNIN	8.3	3.6	1.2	-2.07
HNNCCO	GAQLIV	1.5	3.3	2.2	-1.99
HNCCNN	HURBUR01	9.5	3.6	2.0	-1.71
HOCCCO	YAVROC	4.7	3.4	2.2	-1.58
HNNCCO	ITIJOL01	8.4	3.5	2.6	-1.33
HOCCCO	LEPLIC	5.3	3.3	2.8	-1.29