Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Effect of Substituent and Solvent on Cation-π Interaction in Benzene and Borazine: A Computational Study

Kusum K. Bania*[a] Ankur Kanti Guha*[b], Pradip Kr. Bhattacharyya*[c] and Sourab Sinha[c]

[a]Tezpur University, Napaam, Assam India, 784028,

[b]Dibrugarh University, Dibrugarh, Assam, India, 786004,

[c]Arya Vidyapeeth College, Guwahati, Assam, India, 781016.

Table S1. ΔE_{BSSE} corrections at B3LYP and MP2 level calculation in gas phase

	B3LYP			MP2		
	6-31+G(d)	6-31++G(d,p)	6-311++G(d,p)	6-31+G(d)	6-31++G(d,p)	6-311++G(d,p)
Benzene -Li^+	0.51	0.57	0.56	4.47	4.27	3.90
Benzene -Na^+	0.40	0.50	0.72	3.78	3.70	2.99
Benzene -K^+	0.29	0.3	0.32	2.33	2.62	2.17
Benzene-$(CH_3)_3$-Li^+	0.45	0.57	0.32	2.11	2.94	2.51
Benzene-$(CH_3)_3$-Na^+	0.78	0.78	0.84	4.06	3.68	2.88
Benzene -$(CH_3)_3$-K^+	0.49	0.49	0.37	3.75	3.77	2.43
Benzene-$(NH_2)_3$-Li^+	0.75	0.74	0.69	4.24	3.90	3.65
Benzene-$(NH_2)_3$-Na^+	0.88	0.97	0.89	3.84	3.59	2.91
Benzene -$(NH_2)_3$-K^+	0.64	0.68	0.41	4.29	4.48	2.50
Borazine -Li^+	0.62	0.56	0.40	3.17	2.84	2.22
Borazine -Na^+	0.56	0.58	0.55	2.98	2.68	1.63
Borazine -K^+	0.37	0.37	0.16	2.66	2.83	1.56
Borazine-$(CH_3)_3$-Li^+	0.73	0.65	0.46	3.38	2.97	2.76
Borazine-$(CH_3)_3$-Na^+	0.82	0.77	0.70	3.48	3.12	2.13
Borazine -$(CH_3)_3$-K^+	0.61	0.64	0.23	4.21	4.68	2.25
Borazine -$(NH_2)_3$-Li^+	0.93	0.78	0.66	3.51	3.12	2.86
Borazine-$(NH_2)_3$-Na^+	1.02	0.94	0.82	3.70	3.24	2.28
Borazine -$(NH_2)_3$-K^+	0.63	0.62	0.25	4.19	4.50	2.26
Borazine -$(NO_2)_3$-Li^+	0.64	0.61	0.46	2.93	2.80	2.00
Borazine-$(NO_2)_3$-Na^+	0.63	0.59	0.63	2.14	2.08	1.69
Borazine -$(NO_2)_3$-K^+	0.44	0.46	0.31	2.93	3.02	1.85

Table S2. BSSE corrected cation-π interaction energy (in kcal/mol) of borazine and their substituted derivatives in different solvent medium at B3LYP/6-31++G(d,p) level of calculation.

Compounds	Interaction Energy, ΔE		
	Benzene	Acetone	Water
Borazine -Li^+	-0.95	15.26	16.43
Borazine -Na^+	-1.18	7.80	8.39
Borazine -K^+	-1.56	3.51	3.84
Borazine-$(CH_3)_3$-Li^+	-6.36	12.79	14.24
Borazine-$(CH_3)_3$-Na^+	-4.61	6.58	7.36
Borazine -$(CH_3)_3$-K^+	-2.75	4.25	4.75
Borazine -$(NH_2)_3$-Li^+	-15.54	8.79	10.90
Borazine-$(NH_2)_3$-Na^+	-12.47	3.92	5.36
Borazine -$(NH_2)_3$-K^+	-10.64	0.72	1.77
Borazine -$(NO_2)_3$-Li^+	24.87	26.17	25.47
Borazine-$(NO_2)_3$-Na^+	19.74	15.91	14.90
Borazine -$(NO_2)_3$-K^+	15.43	10.95	10.09

Table S3. Corerelation values (R^2) between Hammet constant (σ_m, σ_p and $\Sigma\sigma_m+\sigma_p$) and interaction energies (ΔE). The values of Hmmmet constants are taken from ref (45). and those of interaction energies

					R^2 values for plot of ΔE against											
					Gas			Benzene			Acetone			Water		
Cation-pi Complexes	Substit -uents	σ_m	σ_p	$\Sigma\sigma_m+\sigma_p$	σ_m	σ_p	$\Sigma\sigma_m+\sigma_p$	σ_m	σ_p	$\Sigma\sigma_m+\sigma_p$	σ_m	σ_p	$\Sigma\sigma_m+\sigma_p$	σ_m	σ_p	$\Sigma\sigma_m+\sigma_p$
Borazine-Li^+	CH_3	-0.07	-0.17	-0.24	0.98	0.98	1	0.98	0.98	0.99	0.98	0.94	0.99	0.99	0.97	0.99
Borazine-Na^+	NH_2	-0.16	-0.66	-0.82	0.97	0.99	0.99	0.98	0.99	1	0.99	0.97	0.98	0.99	0.96	0.99
Borazine-K^+	NO_2	0.71	0.78	1.49	0.96	0.99	0.99	0.03	0.00	0.00	0.99	0.98	0.99	0.99	0.96	0.99

Table S4. NICS values of the cationic complexes of benzene and substituted benzene.

Compound	NICS(0)	NICS(1)
Benzene	-7.9	-10.1
Benzene-Li^+	-7.5	-9.8
Benzene-Na^+	-6.4	-9.7
Benzene-K^+	-7.4	-10.1
Benzene-$(CH_3)_3$	-8.1	-9.4
Benzene-$(CH_3)_3$-Li^+	-7.7	-9.1
Benzene-$(CH_3)_3$-Na^+	-6.2	-8.9
Benzene-$(CH_3)_3$-K^+	-6.9	-8.9
Benzene-$(NH_2)_3$	-7.1	-6.7
Benzene-$(NH_2)_3$-Li^+	-6.1	-5.6
Benzene-$(NH_2)_3$-Na^+	-5.0	-5.4
Benzene-$(NH_2)_3$-K^+	-6.2	-5.9

Table S5. Counterpoised corrected interaction energy of borazine dimer, H_2O linked borazine and its substituted compounds, and M-π-π (M= Li^+, Na^+, K^+) complexes of borazine.

Compounds	ΔEint	ΔE_{BSSE}
Borazine-Borazine	-0.5896	0.42079
Borazine-$(CH_3)_3$-H_2O- Borazine-$(CH_3)_3$	-3.8730	2.31921
Borazine-$(CH_3)_3$-H_2O- Borazine-$(CH_3)_3$	-12.1114	1.67072
Li^+-Borazine-Borazine	-32.7670	1.18913
Na^+-Borazine-Borazine	-20.5961	1.30425
K^+-Borazine-Borazine	-12.7279	0.85684

Table S6. Chemical hardness (η, in a.u.), chemical potential (μ in a.u.) and electrophilicity index (ω) of benzene, borazine and their substituted derivatives in gas phase calculated at B3LYP/6-31++G (d,p).

Compounds	η	μ	ω	Compounds	η	μ	ω
1.Benzene	0.121	-0.136	0.077	**1**.Borazine	0.140	-0.147	0.077
2.Benzene -Li^+	0.125	-0.336	0.451	**2**.Borazine -Li^+	0.147	-0.340	0.393
3.Benzene -Na^+	0.114	-0.320	0.445	**3**.Borazine -Na^+	0.127	-0.335	0.440
4.Benzene -K^+	0.114	-0.300	0.392	**4**.Borazine -K^+	0.127	-0.315	0.389
5.Benzene-$(CH_3)_3$	0.122	-0.113	0.053	**5**.Borazine-$(CH_3)_3$	0.127	-0.143	0.080
6.Benzene -$(CH_3)_3$-Li^+	0.117	-0.305	0.396	**6**.Borazine -$(CH_3)_3$-Li^+	0.138	-0.319	0.368
7.Benzene -$(CH_3)_3$-Na^+	0.102	-0.298	0.435	**7**.Borazine -$(CH_3)_3$-Na^+	0.120	-0.316	0.416
8.Benzene -$(CH_3)_3$-K^+	0.101	-0.284	0.398	**8**.Borazine -$(CH_3)_3$-K^+	0.122	-0.299	0.365
9.Benzene -$(NH_2)_3$	0.090	-0.104	0.060	**9**.Borazine -$(NH_2)_3$	0.102	-0.268	0.350
10.Benzene -$(NH_2)_3$-Li^+	0.100	-0.265	0.349	**10**.Borazine -$(NH_2)_3$-Li^+	0.115	-0.281	0.343
11.Benzene-$(NH_2)_3$-Na^+	0.084	-0.265	0.416	**11**.Borazine -$(NH_2)_3$-Na^+	0.101	-0.281	0.390
12.Benzene -$(NH_2)_3$-K^+	0.087	-0.250	0.360	**12**.Borazine -$(NH_2)_3$-K^+	0.102	-0.268	0.350
				13. Borazine-$(NO_2)_3$	0.095	-0.241	0.305
				14.Borazine -$(NO_2)_3$-Li^+	0.087	-0.369	0.778
				15.Borazine -$(NO_2)_3$-Na^+	0.087	-0.379	0.820
				16.Borazine -$(NO_2)_3$-K^+	0.088	-0.358	0.723

Table S7. Chemical hardness (η, in a.u.), chemical potential (μ in a.u.) and electrophilicity index (ω) of benzene, borazine and their substituted derivatives in gas phase calculated at B3LYP/6-311++G (d,p).

Compounds	η	μ	ω	Compounds	η	μ	ω
1.Benzene	0.121	-0.135	0.075	**1**.Borazine	0.143	-0.143	0.072
2.Benzene -Li^+	0.117	-0.307	0.402	**2**.Borazine -Li^+	0.147	-0.340	0.392
3.Benzene -Na^+	0.102	-0.300	0.438	**3**.Borazine -Na^+	0.127	-0.335	0.439
4.Benzene -K^+	0.103	-0.284	0.393	**4**.Borazine -K^+	0.127	-0.314	0.389
5.Benzene-$(CH_3)_3$	0.114	-0.121	0.064	**5**.Borazine-$(CH_3)_3$	0.127	-0.142	0.079
6.Benzene -$(CH_3)_3$-Li^+	0.125	-0.339	0.459	**6**.Borazine -$(CH_3)_3$-Li^+	0.138	-0.319	0.368
7.Benzene -$(CH_3)_3$-Na^+	0.111	-0.322	0.451	**7**.Borazine -$(CH_3)_3$-Na^+	0.120	-0.316	0.416
8.Benzene -$(CH_3)_3$-K^+	0.116	-0.300	0.387	**8**.Borazine -$(CH_3)_3$-K^+	0.122	-0.299	0.365
9.Benzene -$(NH_2)_3$	0.095	-0.098	0.051	**9**.Borazine -$(NH_2)_3$	0.102	-0.267	0.349
10.Benzene -$(NH_2)_3$-Li^+	0.102	-0.265	0.346	**10**.Borazine -$(NH_2)_3$-Li^+	0.115	-0.280	0.343
11.Benzene-$(NH_2)_3$-Na^+	0.084	-0.266	0.419	**11**.Borazine -$(NH_2)_3$-Na^+	0.101	-0.281	0.389
12.Benzene -$(NH_2)_3$-K^+	0.089	-0.251	0.354	**12**.Borazine -$(NH_2)_3$-K^+	0.102	-0.267	0.349
				13. Borazine-$(NO_2)_3$	0.095	-0.240	0.305
				14.Borazine -$(NO_2)_3$-Li^+	0.087	-0.369	0.777
				15.Borazine -$(NO_2)_3$-Na^+	0.087	-0.379	0.819
				16.Borazine -$(NO_2)_3$-K^+	0.088	-0.358	0.723

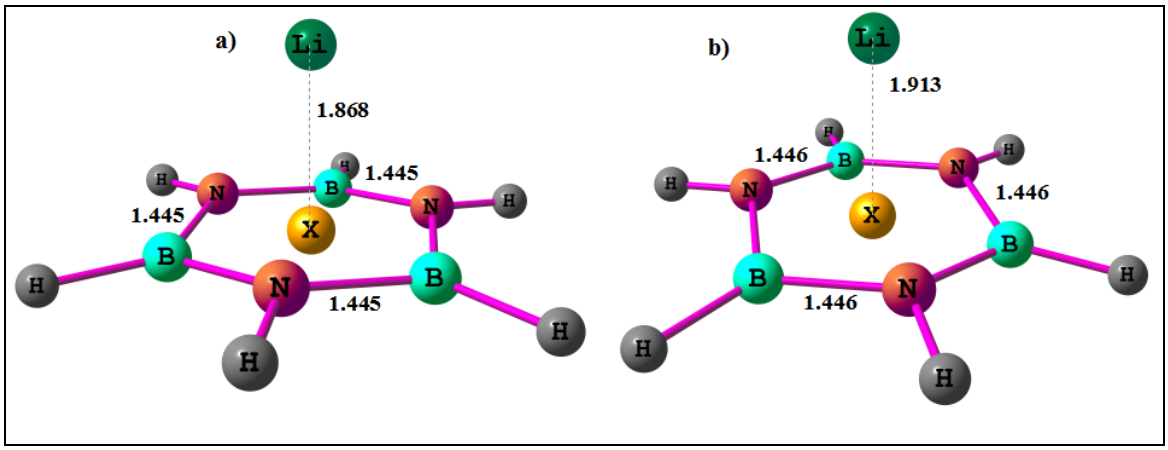

Figure S1. Optimized geometry of $B_3N_3H_6$-Li^+ complex at a) MP2/Aug-ccPVTZ and b) MP2/TZVP level of theory.

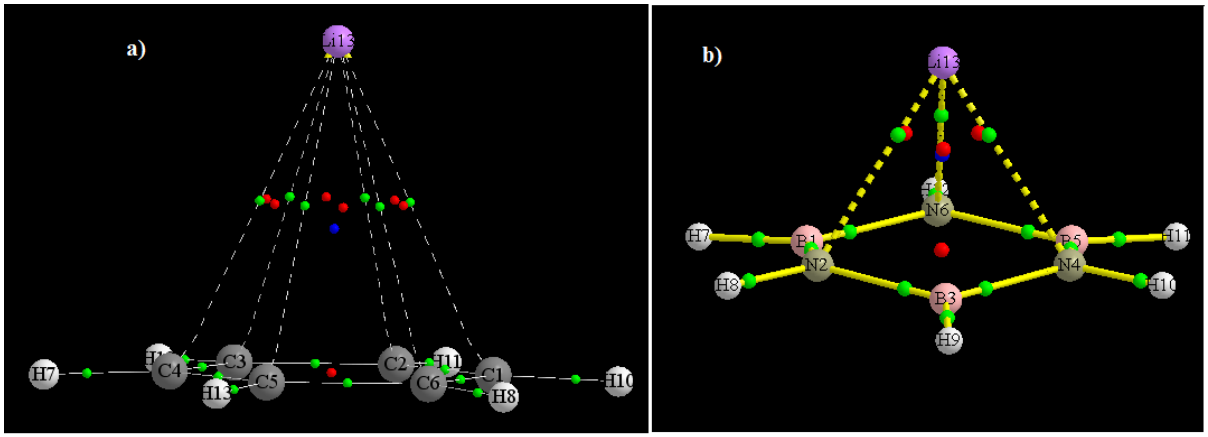

Figure S2. Molecular graph of (a) benzene-Li^+ and (b) borazine-Li^+ complex.

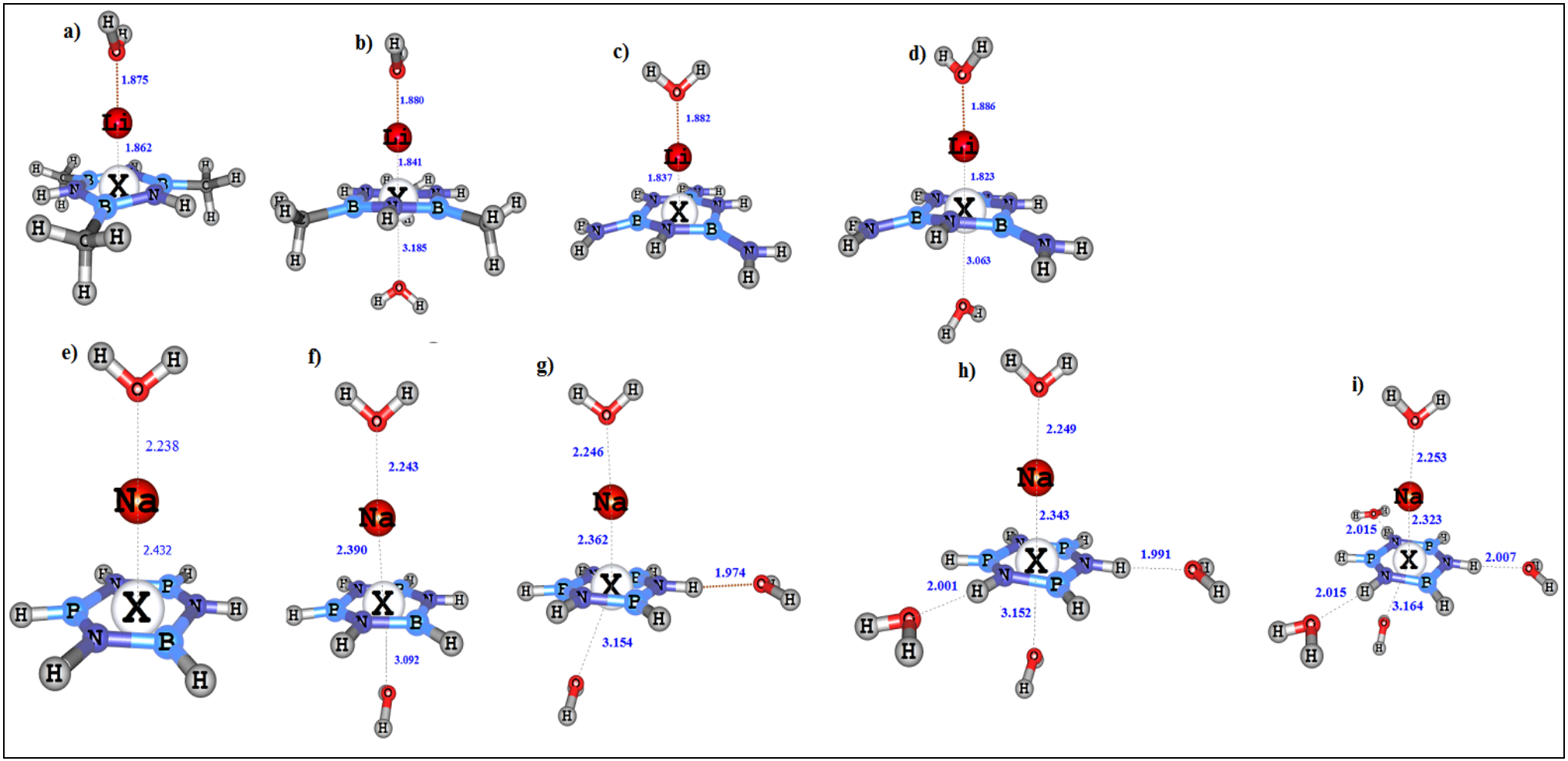

Figure S3. Optimized geometry of a) Borazine $(CH_3)_3$-Li^+-π-W b) Borazine $(CH_3)_3$-Li^+-π-2W c) Borazine $(NH_2)_3$-Li^+-π-W d) Borazine $(NH_2)_3$-Li^+-π-2W e) Borazine-Na^+-π-W f) Borazine-Na^+-π-2W g) Borazine-Na^+-π-3W h) Borazine-Na^+-π-4W i) Borazine-Na^+-π-5W.

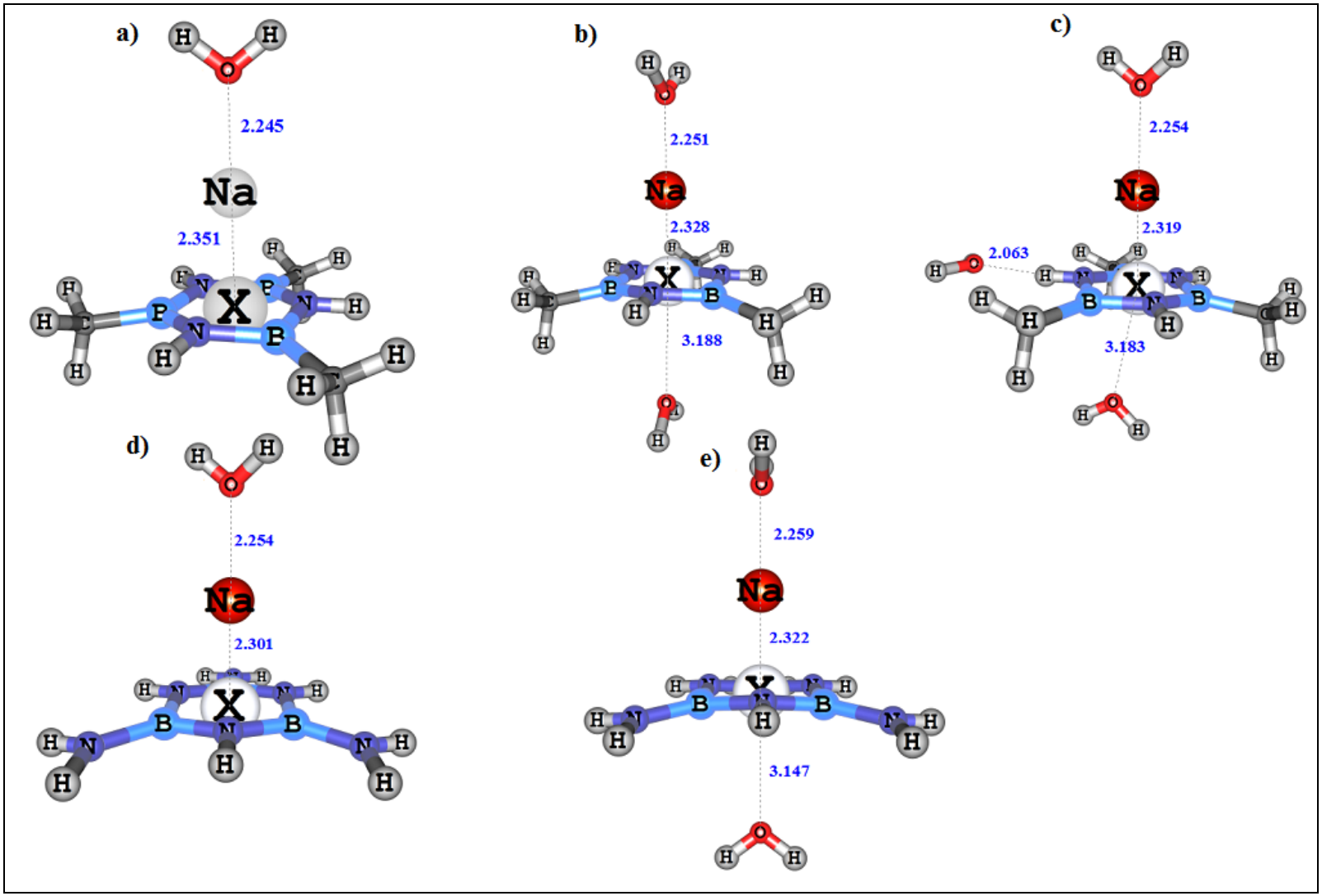

Figure S4. Optimized geometry of a) Borazine $(CH_3)_3$-Na^+-π-W b) Borazine $(CH_3)_3$-Na^+-π-2W c) Borazine $(CH_3)_3$-Na^+-3π-W d) Borazine $(NH_2)_3$-Na^+-π-W e) Borazine $(NH_2)_3$-Na^+-π-2W.

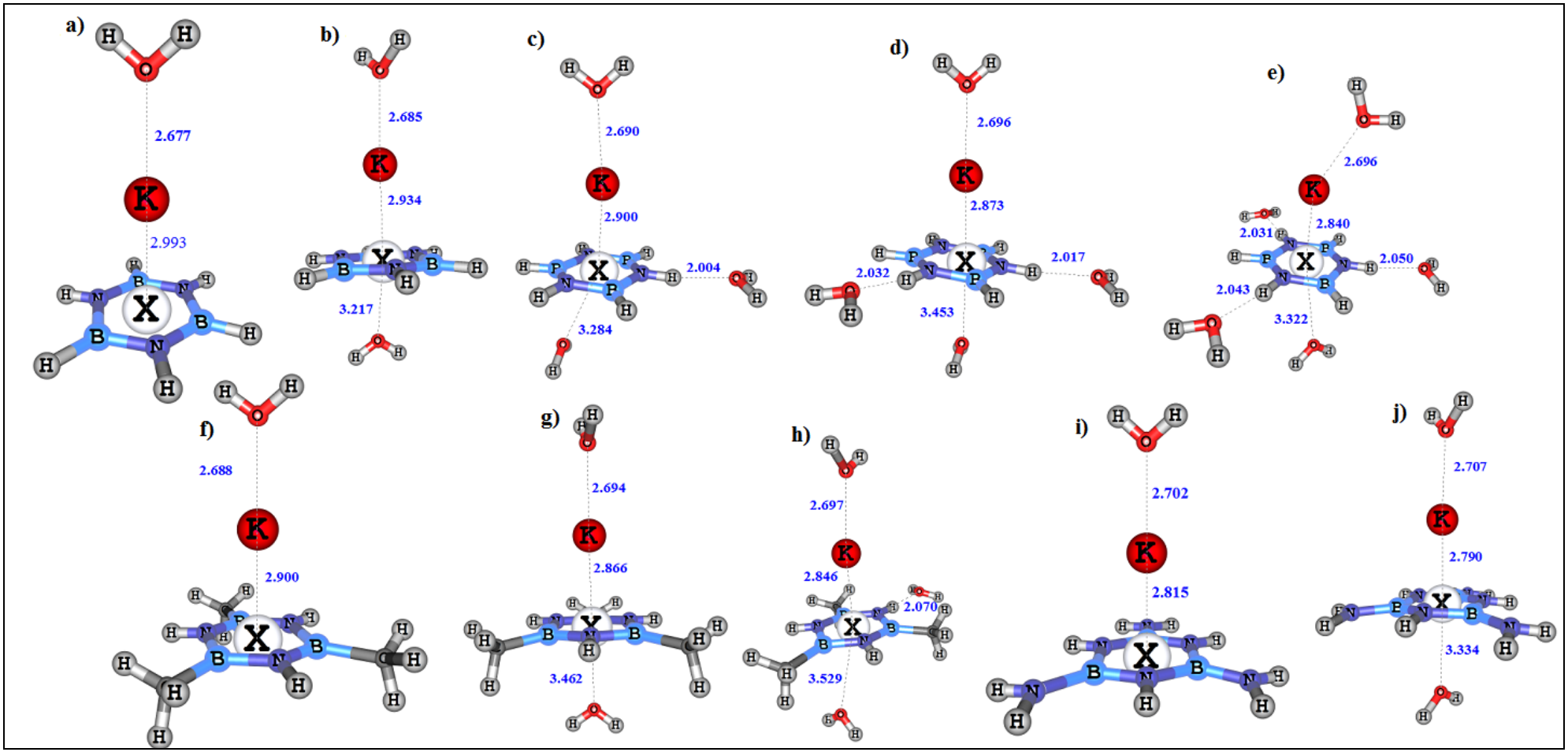

Figure S5. Optimized geometry of a) Borazine-K^+-π-W b) Borazine-K^+-π-2W c) Borazine-K^+-π-3W d) Borazine-K^+-π-4W e) Borazine-K^+-π-5W f) Borazine $(CH_3)_3$-K^+-π-W g) Borazine $(CH_3)_3$-K^+-π-2W h) Borazine $(CH_3)_3$-K^+-π-2W i) Borazine $(NH_2)_3$-K^+-π-W j) Borazine $(NH_2)_3$-K^+-π-2W.

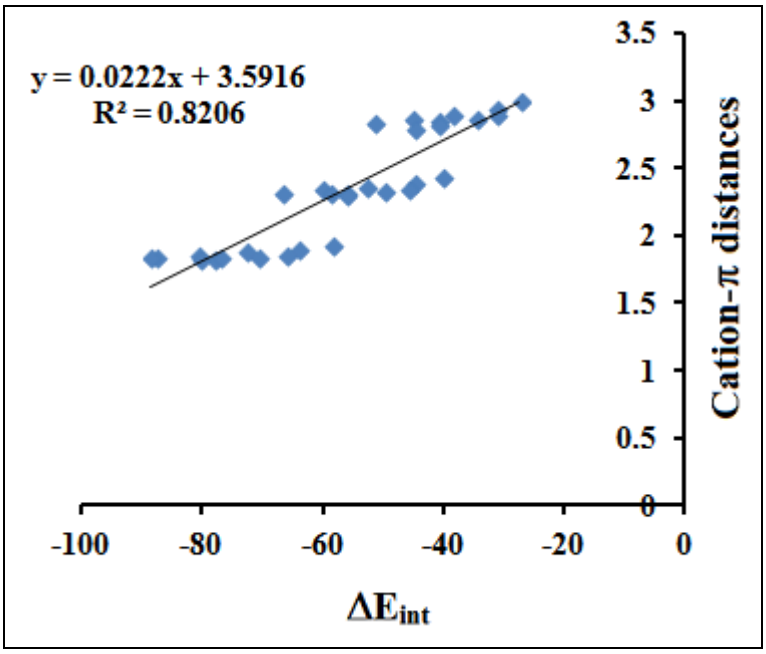

Figure S6. Correlation plot between interaction energies (x-axis) with cation-π distance (y-axis) (Table 7).

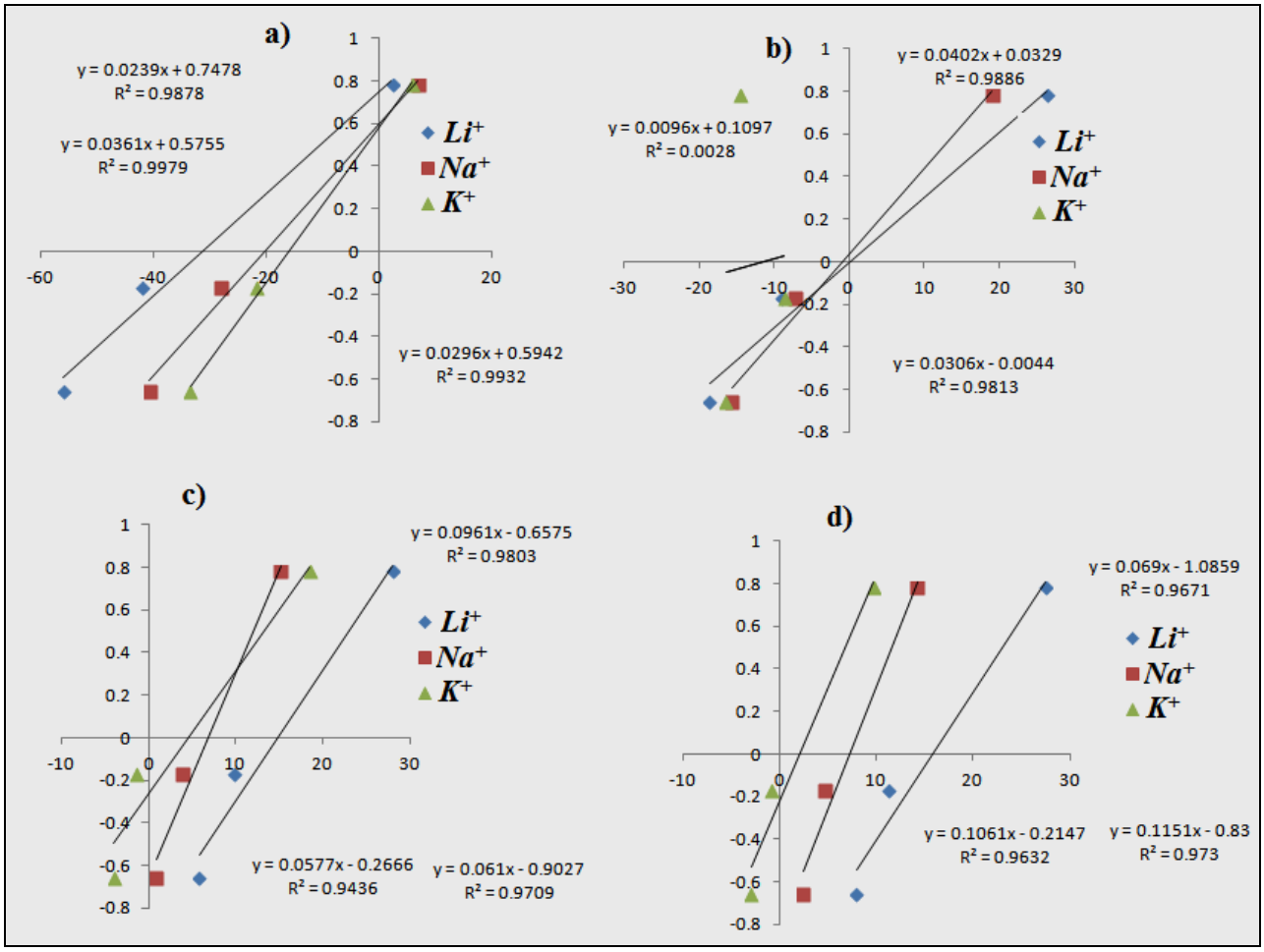

Figure S7. Correlation plot between interaction energies (x-axis) of various substituted cation-π complexes of borazine (Table 5) and Hammet constant (σ_p, y-axis) in a) gas phase b) in benzene medium c) in acetone medium and d) in water medium.

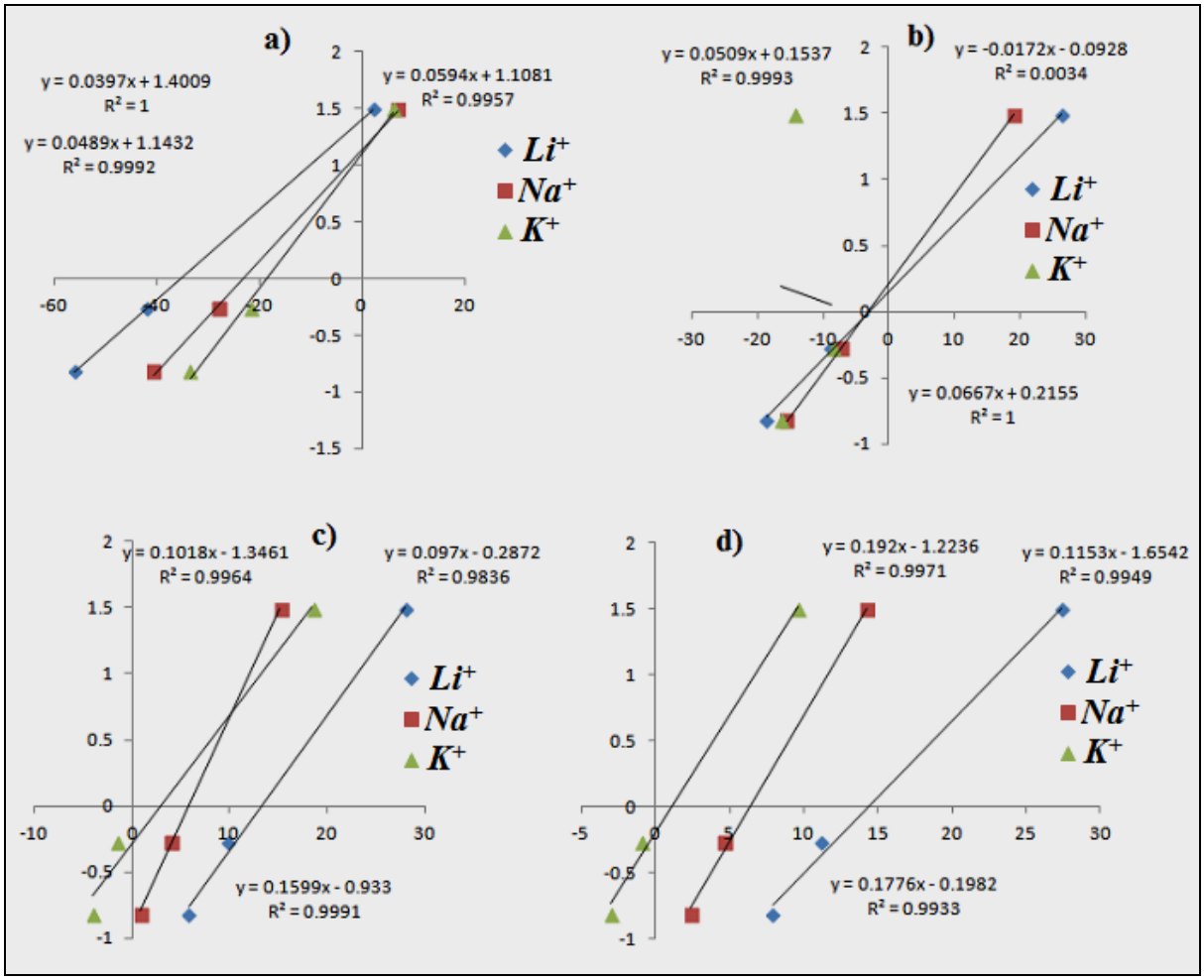

Figure S8. Correlation plot between interaction energies (X-axis) of various substituted cation-π complexes of borazine (Table 5) and Hammet constant ($\sigma Total = (\Sigma\sigma_m + \Sigma\sigma_p)$. , y-axis) in a) gas phase b) in benzene medium c) in acetone medium and d) in water medium.