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

Supporting Information: Substituent Effects in the So-Called Cation$\cdots\pi$ Interaction of Benzene and its Boron-Nitrogen Doped Analogues: Overlooked Role of σ-Skeleton

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Note: energies in tables and figures are in kcal/mol and delocalization indices are in a.u.

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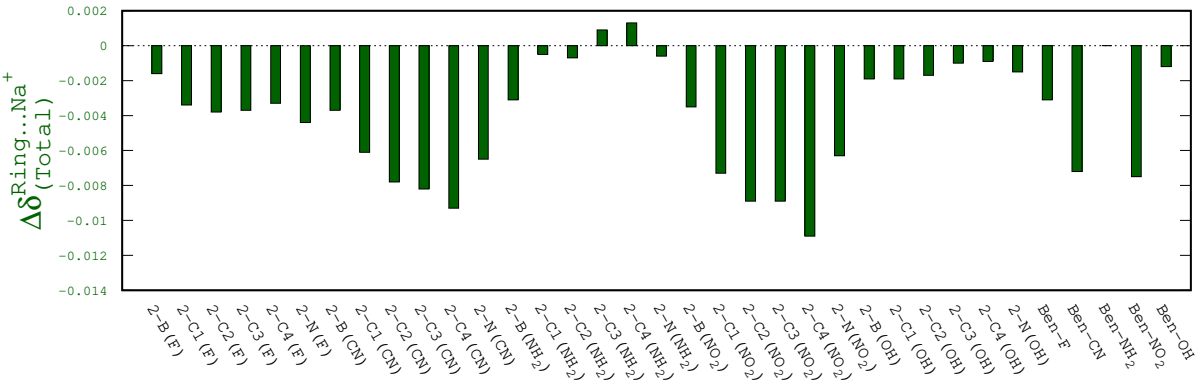


Figure SF1: Changes in the delocalization index (in a.u.) due of the 1,2-azaborine and benzene rings with Na^+ calculated from the total density ($\rho_{(\sigma+\pi+Na^+)} = \rho_\sigma + \rho_\pi + \rho_{Na^+}$) due to the *through-bond* effects (inductive and resonance effects).

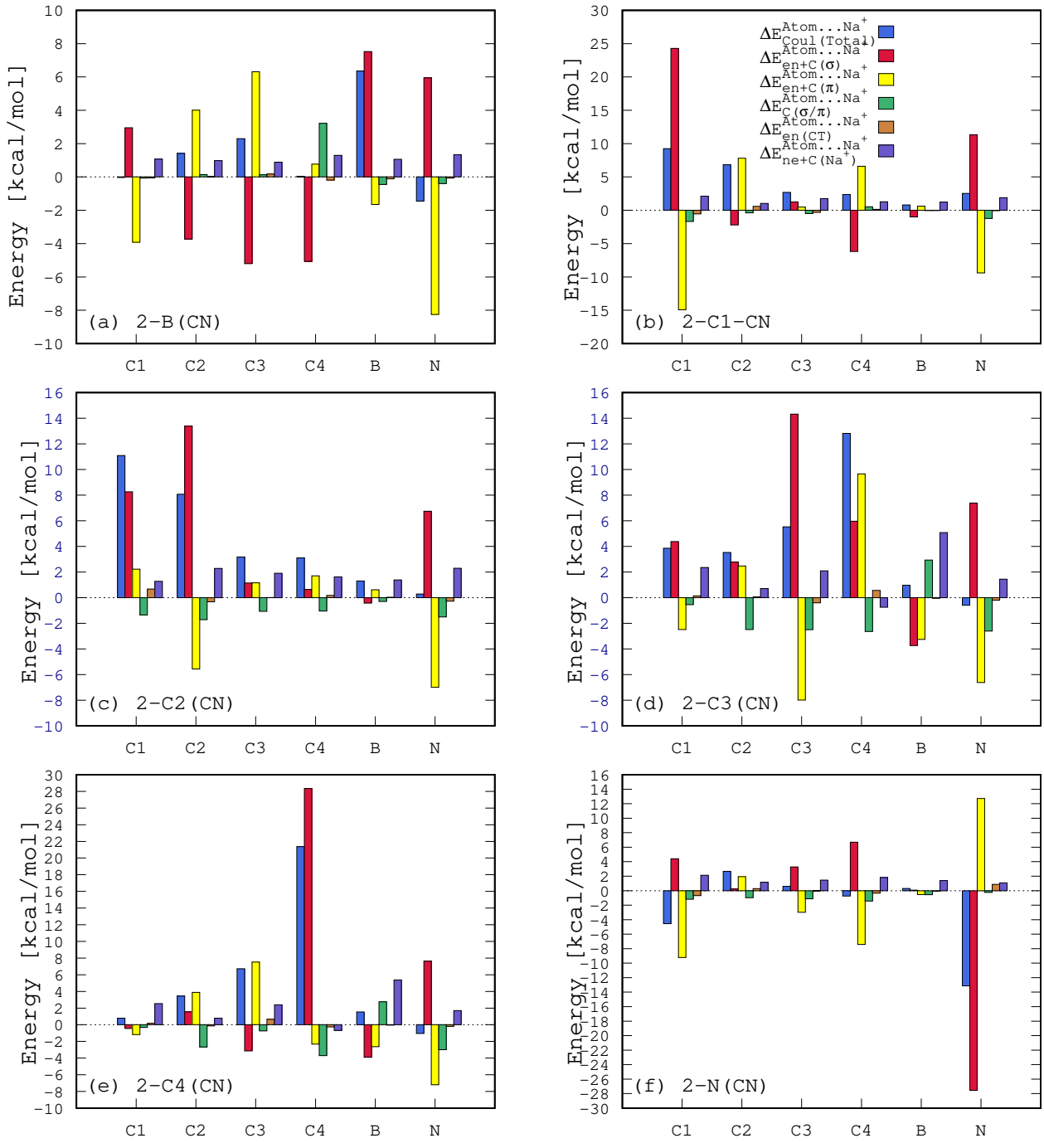


Figure SF2: Atom-cation contributions to the changes for the IQA total Coulomb interaction energy and its components for the case of ring atoms of the cyano-substituted 1,2-azaborines: (a) 2-B(CN), (b) 2-C1(CN), (c) 2-C2(CN), (d) 2-C3(CN), (e) 2-C4(CN), and (f) 2-N(CN).

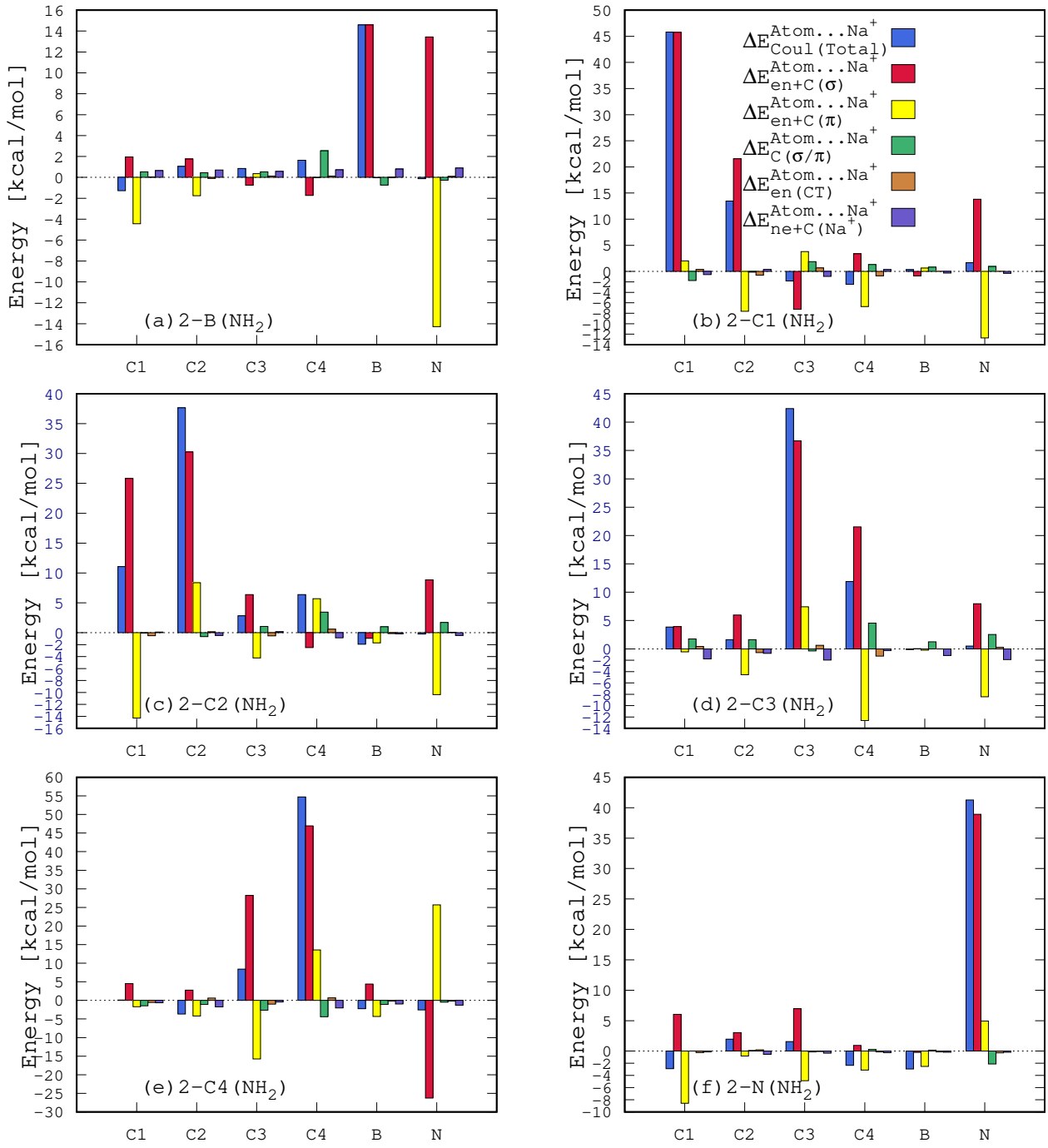


Figure SF3: Atom-cation contributions to the changes for the IQA total Coulomb interaction energy and its components for the case of ring atoms of the amino-substituted 1,2-azaborines: (a) 2-B(NH_2), (b) 2-C1(NH_2), (c) 2-C2(NH_2), (d) 2-C3(NH_2), (e) 2-C4(NH_2), and (f) 2-N(NH_2).

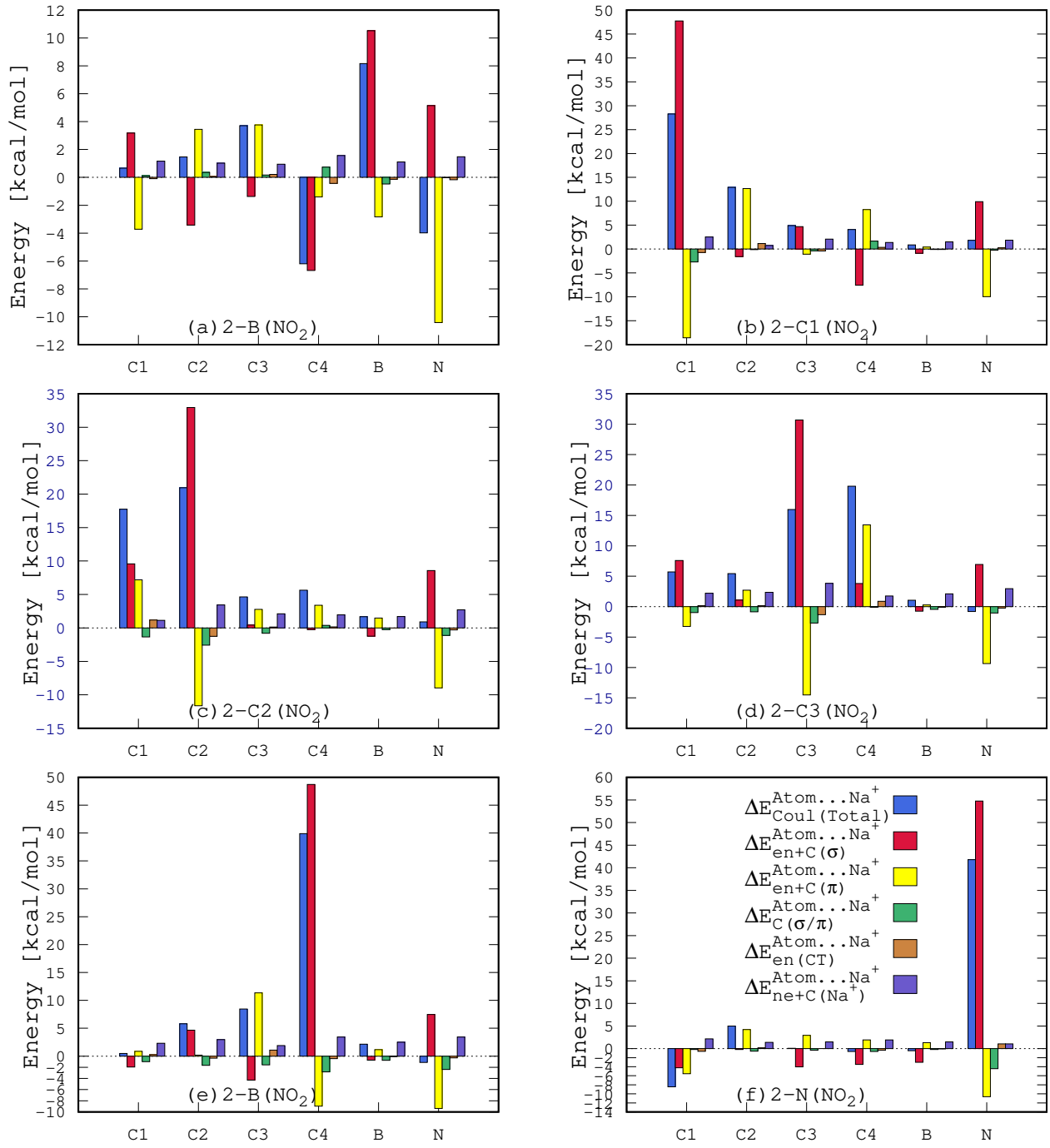


Figure SF4: Atom-cation contributions to the changes for the IQA total Coulomb interaction energy and its components for the case of ring atoms of the nitro-substituted 1,2-azaborines: (a) 2-B(NO_2), (b) 2-C1(NO_2), (c) 2-C2(NO_2), (d) 2-C3(NO_2), (e) 2-C4(NO_2), and (f) 2-N(NO_2).

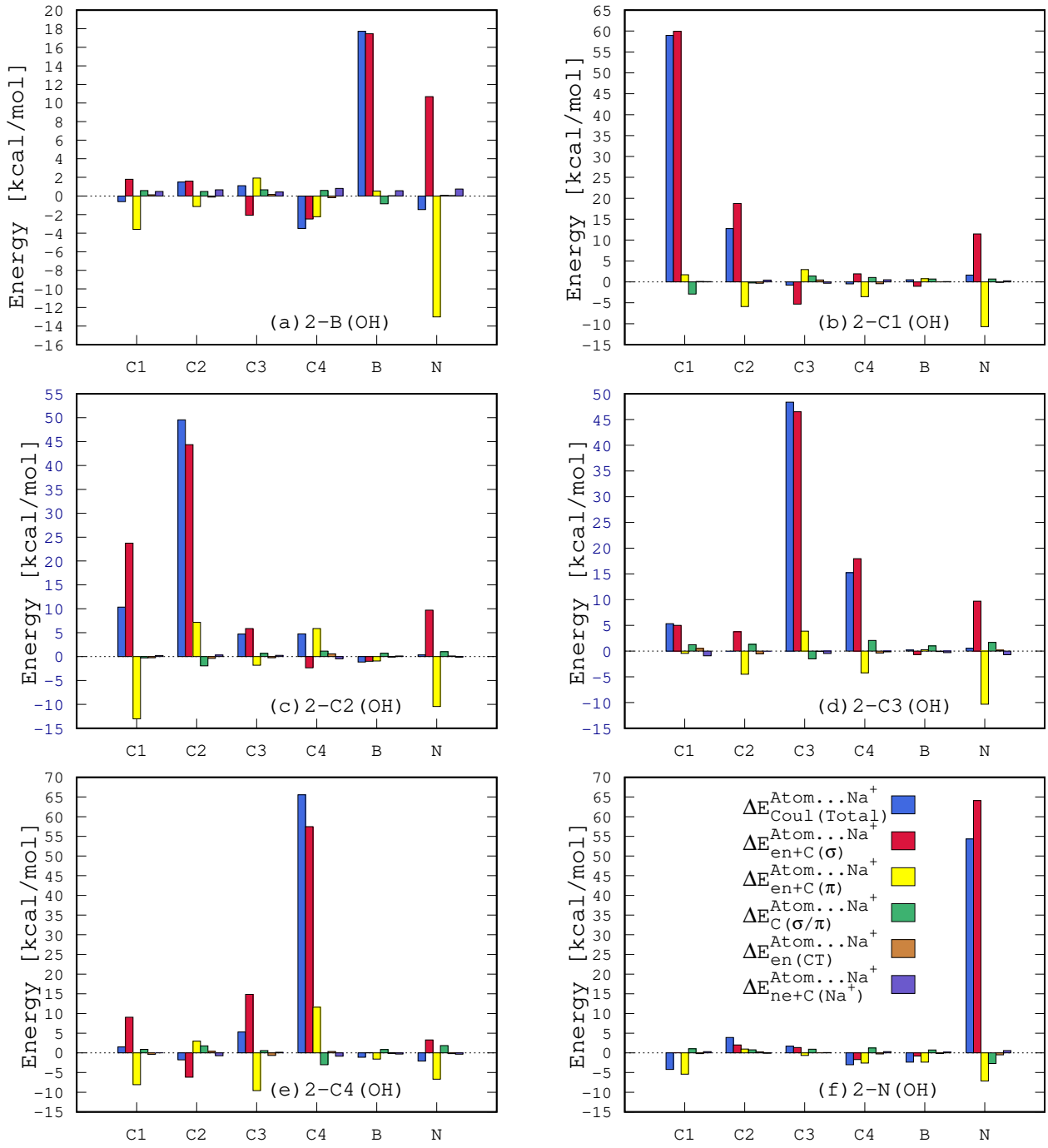
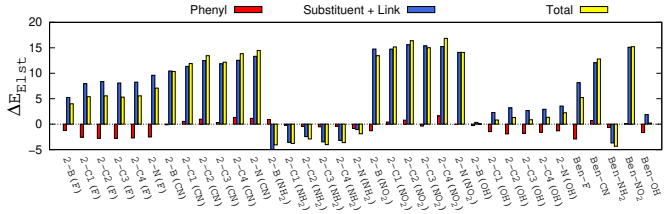


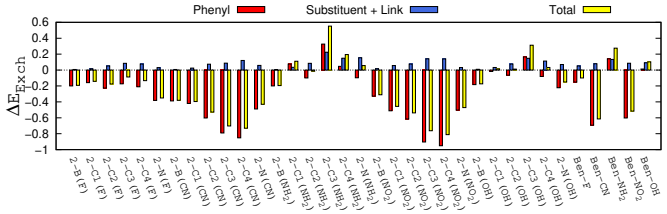
Figure SF5: Atom-cation contributions to the changes for the IQA total Coulomb interaction energy and its components for the case of ring atoms of the hydroxy-substituted 1,2-azaborines: (a) 2-B(OH), (b) 2-C1(OH), (c) 2-C2(OH), (d) 2-C3(OH), (e) 2-C4(OH), and (f) 2-N(OH).

Figure SF6: Difference F-SAPT/jun-cc-pVDZ analysis for the considered systems – less important contributions not included in the main text. Energies are in kcal/mol.

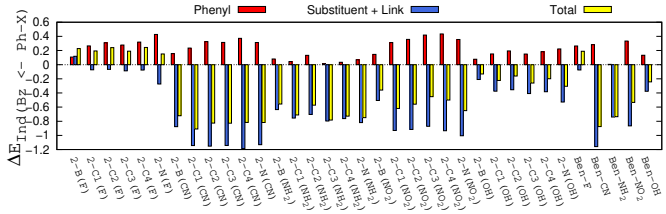
(a) ΔE_{Elst}



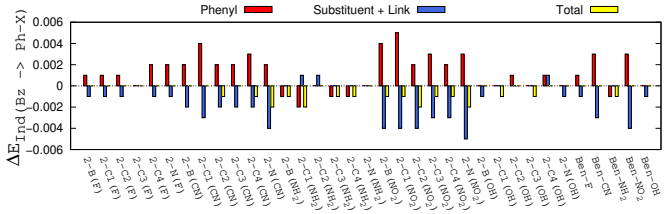
(b) ΔE_{Exch}



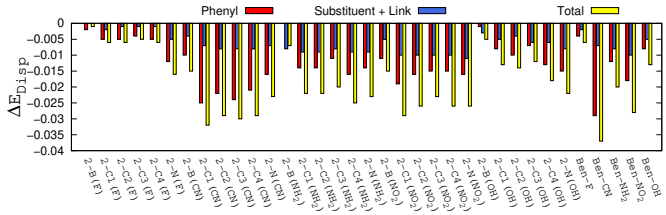
(c) $\Delta E_{Ind}(Ring - X \leftarrow Na^+)$



(d) $\Delta E_{Ind}(Ring - X \rightarrow Na^+)$



(e) ΔE_{Disp}



(f) ΔE_{Tot}

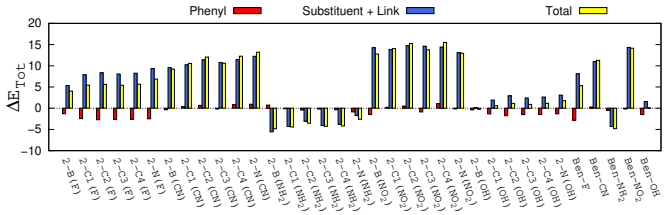


Table ST1: IQA components of complexes of the fluoro-substituted 1,2-azaborines with Na^+ calculated from the total (σ+π+Na^+) HF densities.

	Ring$\cdots Na^+$								$\sum$H$\cdots Na^+$						X$\cdots Na^+$						Total			
Complexes	$E_{int}^{Ring\cdots Na^+}$	$E_{Cl}^{Ring\cdots Na^+}$	$E_{ne+C}^{Ring\cdots Na^+}$	$E_{en}^{Ring\cdots Na^+}$	$E_{C}^{Ring\cdots Na^+}$	$E_{nn}^{Ring\cdots Na^+}$	$E_{XC}^{Ring\cdots Na^+}$	δ(Ring, Na^+)	$\sum E_{int}^{H\cdots Na^+}$	$\sum E_{Cl}^{H\cdots Na^+}$	$\sum E_{ne+C}^{H\cdots Na^+}$	$\sum E_{nn}^{H\cdots Na^+}$	$\sum E_{XC}^{H\cdots Na^+}$	δ(H, Na^+)	$E_{int}^{F\cdots Na^+}$	$E_{Cl}^{F\cdots Na^+}$	$E_{ne+C}^{F\cdots Na^+}$	$E_{nn}^{F\cdots Na^+}$	$E_{XC}^{F\cdots Na^+}$	δ(F, Na^+)	E_{int}^{Tot}	E_{Cl}^{Tot}	E_{XC}^{Tot}	δ(aza, Na^+)
2$\cdots Na^+$	-46.07	-29.80	-47280.08	-90794.08	43514.00	47250.28	-16.28	0.1584	4.78	5.05	-6321.61	6326.66	-0.27	0.0045							-41.30	-24.75	-16.55	0.1629
2$\cdots Na^+$(2.6 Å)	62.22	73.47	-44381.09	-85348.08	40966.99	44454.56	-11.25	0.1186	1.53	1.74	-6075.44	6077.18	-0.20	0.0035							63.75	1.74	75.21	0.1221
2-B(F)$\cdots Na^+$(2.6 Å)	97.32	108.48	-44346.08	-85188.67	40842.59	44454.56	-11.16	0.1171	69.91	70.04	-5027.89	5097.93	-0.13	0.0023	-78.47	-78.42	-8623.52	8545.10	-0.05	0.0009	88.76	100.10	-11.34	0.1203
2-Cl(F)$\cdots Na^+$	33.51	49.55	-47200.74	-89894.25	42693.51	47250.28	-16.04	0.1550	2.69	2.93	-5261.36	5264.29	-0.23	0.0039	-70.22	-70.13	-9129.14	9059.01	-0.09	0.0015	-34.01	-17.65	-16.36	0.1604
2-C2(F)$\cdots Na^+$	27.69	43.70	-47206.59	-89934.09	42727.51	47250.28	-16.01	0.1546	6.01	6.23	-5257.02	5263.24	-0.22	0.0036	-69.77	-69.65	-9116.48	9046.83	-0.12	0.0020	-36.07	-19.72	-16.34	0.1601
2-C3(F)$\cdots Na^+$	29.35	45.42	-47204.87	-89942.73	42737.86	47250.28	-16.06	0.1547	6.37	6.60	-5261.76	5268.36	-0.22	0.0036	-69.70	-69.57	-9080.89	9011.32	-0.13	0.0022	-33.97	-17.56	-16.42	0.1605
2-C4(F)$\cdots Na^+$	25.80	41.89	-47208.40	-89958.65	42750.25	47250.28	-16.09	0.1551	7.00	7.22	-5272.79	5280.00	-0.21	0.0034	-68.95	-68.80	-8971.17	8902.38	-0.15	0.0026	-36.14	-19.69	-16.45	0.1611
2-N(F)$\cdots Na^+$	25.09	41.05	-47209.24	-89963.47	42754.22	47250.28	-15.96	0.1540	-28.72	-28.48	-5276.18	5247.70	-0.24	0.0040	-31.53	-31.47	-9008.93	8977.46	-0.06	0.0011	-35.17	-18.91	-16.26	0.1591

Table ST2: IQA components of complexes of the fluoro-substituted 1,2-azaborines with Na^+ calculated from the σ, π, and Na^+ parts of the total HF densities.

	σ		π		σ/π		cation		
Complexes	$E^{Ring\cdots Na^+}_{ne+C(\sigma)}$	$E^{Ring\cdots Na^+}_{XC(\sigma)}$	$E^{Ring\cdots Na^+}_{ne+C(\pi)}$	$E^{Ring\cdots Na^+}_{XC(\pi)}$	$E^{Ring\cdots Na^+}_{C(\sigma/\pi)}$	$E^{Ring\cdots Na^+}_{XC(\sigma/\pi)}$	$E^{Ring\cdots Na^+}_{ne+C(Na^+)}$	$E^{Ring\cdots Na^+}_{XC(Na^+)}$	$E^{Ring\cdots Na^+}_{en(CT)}$
$2\cdots Na^+$	-3647.04	-1.18	-684.31	-8.84	248.99	-1.47	-43150.38	-4.79	-46.83
$2\cdots Na^+$(2.6 Å)	-3417.79	-0.62	-656.28	-6.93	285.82	-0.76	-40563.36	-2.95	-29.02
2-B(F)$\cdots Na^+$(2.6 Å)	-3395.63	-0.58	-665.76	-6.92	304.77	-0.69	-40559.76	-2.97	-29.26
2-C1(F)$\cdots Na^+$	-3559.12	-0.98	-696.68	-9.13	248.18	-1.16	-43145.95	-4.77	-46.66
2-C2(F)$\cdots Na^+$	-3563.79	-0.97	-696.80	-9.12	246.44	-1.15	-43145.31	-4.77	-46.63
2-C3(F)$\cdots Na^+$	-3562.87	-0.99	-696.96	-9.05	247.96	-1.21	-43145.40	-4.81	-47.09
2-C4(F)$\cdots Na^+$	-3570.09	-1.51	-676.66	-7.94	232.76	-1.84	-43146.99	-4.79	-46.91
2-N(F)$\cdots Na^+$	-3564.87	-0.99	-697.92	-9.06	244.27	-1.15	-43143.78	-4.75	-46.44

Table ST3: IQA components of complexes of the cyano-substituted 1,2-azaborines with Na^+ calculated from the total (σ+π+Na^+) HF densities.

	Ring$\cdots Na^+$								$\sum$H$\cdots Na^+$						CN$\cdots Na^+$						Total			
Complexes	$E_{int}^{Ring\cdots Na^+}$	$E_{Cl}^{Ring\cdots Na^+}$	$E_{ne+C}^{Ring\cdots Na^+}$	$E_{en}^{Ring\cdots Na^+}$	$E_{C}^{Ring\cdots Na^+}$	$E_{nn}^{Ring\cdots Na^+}$	$E_{XC}^{Ring\cdots Na^+}$	δ(Ring, Na^+)	$\sum E_{int}^{H\cdots Na^+}$	$\sum E_{Cl}^{H\cdots Na^+}$	$\sum E_{ne+C}^{H\cdots Na^+}$	$\sum E_{nn}^{H\cdots Na^+}$	$\sum E_{XC}^{H\cdots Na^+}$	δ(H, Na^+)	$E_{int}^{CN\cdots Na^+}$	$E_{Cl}^{CN\cdots Na^+}$	$E_{ne+C}^{CN\cdots Na^+}$	$E_{nn}^{CN\cdots Na^+}$	$E_{XC}^{CN\cdots Na^+}$	δ(CN, Na^+)	E_{int}^{Tot}	E_{Cl}^{Tot}	E_{XC}^{Tot}	δ(aza, Na^+)
2-B(CN)$\cdots Na^+$	-37.17	-21.16	-47271.45	-90723.05	43451.59	47250.28	-16.01	0.1547	78.01	78.18	-5231.52	5309.71	-0.16	0.0029	-71.33	-71.20	-11031.64	10960.43	-0.13	0.0020	-30.49	-14.19	-16.30	0.1595
2-C1(CN)$\cdots Na^+$	-21.13	-5.33	-47255.61	-90507.92	43252.31	47250.28	-15.80	0.1523	4.12	4.34	-5259.95	5264.29	-0.22	0.0037	-14.76	-14.66	-11444.83	11430.18	-0.10	0.0020	-31.77	-15.66	-16.12	0.1580
2-C2(CN)$\cdots Na^+$	-18.43	-2.79	-47253.07	-90468.68	43215.60	47250.28	-15.64	0.1506	7.91	8.12	-5255.12	5263.24	-0.21	0.0034	-20.25	-20.12	-11458.96	11438.84	-0.13	0.0026	-30.78	-14.79	-15.99	0.1565
2-C3(CN)$\cdots Na^+$	-19.29	-3.67	-47253.95	-90494.12	43240.16	47250.28	-15.62	0.1502	6.98	7.19	-5261.17	5268.36	-0.21	0.0035	-18.10	-17.97	-11398.58	11380.61	-0.14	0.0027	-30.42	-14.44	-15.97	0.1564
2-C4(CN)$\cdots Na^+$	-12.54	3.04	-47247.25	-90432.20	43184.95	47250.28	-15.54	0.1491	8.92	9.12	-5260.57	5280.00	-0.19	0.0031	-23.74	-23.57	-11301.49	11277.92	-0.17	0.0034	-27.32	-11.41	-15.91	0.1556
2-N(CN)$\cdots Na^+$	-60.41	-44.67	-47294.95	-90956.18	43661.23	47250.28	-15.74	0.1519	-29.20	-28.97	-5276.66	5247.69	-0.23	0.0039	60.18	60.25	-11563.66	11623.92	-0.07	0.0015	-29.43	-13.39	-16.05	0.1573

Table ST4: IQA components of complexes of the cyano-substituted 1,2-azaborines with Na^+ calculated from the σ, π, and Na^+ parts of the total HF densities.

	σ		π		σ/π		cation		
Complexes	$E^{Ring\cdots Na^+}_{ne+C(\sigma)}$	$E^{Ring\cdots Na^+}_{XC(\sigma)}$	$E^{Ring\cdots Na^+}_{ne+C(\pi)}$	$E^{Ring\cdots Na^+}_{XC(\pi)}$	$E^{Ring\cdots Na^+}_{C(\sigma/\pi)}$	$E^{Ring\cdots Na^+}_{XC(\sigma/\pi)}$	$E^{Ring\cdots Na^+}_{ne+C(Na^+)}$	$E^{Ring\cdots Na^+}_{XC(Na^+)}$	$E^{Ring\cdots Na^+}_{en(CT)}$
2-B(CN)$\cdots Na^+$	-3644.63	-0.95	-687.04	-8.92	251.56	-1.32	-43143.76	-4.81	-47.08
2-C1(CN)$\cdots Na^+$	-3619.55	-0.96	-693.13	-8.90	245.69	-1.13	-43141.08	-4.81	-47.05
2-C2(CN)$\cdots Na^+$	-3617.29	-1.00	-691.18	-8.73	242.01	-1.16	-43139.60	-4.75	-46.52
2-C3(CN)$\cdots Na^+$	-3615.95	-0.99	-692.53	-8.66	241.17	-1.20	-43139.43	-4.77	-46.71
2-C4(CN)$\cdots Na^+$	-3618.31	-0.96	-687.58	-8.58	242.68	-1.24	-43136.91	-4.76	-46.63
2-N(CN)$\cdots Na^+$	-3659.92	-1.05	-689.80	-8.54	243.43	-1.37	-43141.33	-4.78	-46.83

Table ST5: IQA components of complexes of the amino-substituted 1,2-azaborines with Na^+ calculated from the total (σ+π+Na^+) HF densities.

	Ring$\cdots Na^+$								$\sum$H$\cdots Na^+$						$NH_2\cdots Na^+$						Total			
Complexes	$E_{int}^{Ring\cdots Na^+}$	$E_{Cl}^{Ring\cdots Na^+}$	$E_{ne+C}^{Ring\cdots Na^+}$	$E_{en}^{Ring\cdots Na^+}$	$E_{C}^{Ring\cdots Na^+}$	$E_{nn}^{Ring\cdots Na^+}$	$E_{XC}^{Ring\cdots Na^+}$	δ(Ring, Na^+)	$\sum E_{int}^{H\cdots Na^+}$	$\sum E_{Cl}^{H\cdots Na^+}$	$\sum E_{ne+C}^{H\cdots Na^+}$	$\sum E_{nn}^{H\cdots Na^+}$	$\sum E_{XC}^{H\cdots Na^+}$	δ(H, Na^+)	$E_{int}^{NH_2\cdots Na^+}$	$E_{Cl}^{NH_2\cdots Na^+}$	$E_{ne+C}^{NH_2\cdots Na^+}$	$E_{nn}^{NH_2\cdots Na^+}$	$E_{XC}^{NH_2\cdots Na^+}$	δ(NH_2, Na^+)	E_{int}^{Tot}	E_{Cl}^{Tot}	E_{XC}^{Tot}	δ(aza, Na^+)
2-B(NH_2)$\cdots Na^+$	-29.11	-13.04	-47263.33	-90618.60	43355.26	47250.28	-16.06	0.1553	65.96	66.14	-5243.56	5309.70	-0.18	0.0032	-80.49	-80.33	-8563.71	8483.37	-0.16	0.0023	-43.64	-27.24	-16.40	0.1608
2-C1(NH_2)$\cdots Na^+$	10.88	27.19	-47223.09	-90132.43	42909.33	47250.28	-16.32	0.1579	-8.87	-8.61	-5272.90	5264.29	-0.29	0.0042	-48.21	-48.09	-8750.41	8702.32	-0.12	0.0020	-46.20	-29.51	-16.69	0.1642
2-C2(NH_2)$\cdots Na^+$	9.69	25.99	-47224.29	-90167.88	42943.58	47250.28	-16.29	0.1577	-4.71	-4.47	-5267.72	5263.24	-0.24	0.0040	-47.33	-47.19	-8734.53	8687.34	-0.14	0.0026	-42.35	-25.68	-16.67	0.1643
2-C3(NH_2)$\cdots Na^+$	13.88	30.38	-47219.90	-90140.53	42920.63	47250.28	-16.50	0.1593	-6.07	-5.81	-5274.18	5268.36	-0.25	0.0041	-51.40	-51.21	-8744.30	8693.08	-0.19	0.0037	-43.58	-26.65	-16.93	0.1671
2-C4(NH_2)$\cdots Na^+$	8.49	24.95	-47225.33	-90163.21	42937.88	47250.28	-16.47	0.1597	-3.70	-3.46	-5283.46	5280.00	-0.24	0.0039	-51.52	-51.33	-8644.09	8592.76	-0.19	0.0036	-46.73	-29.83	-16.90	0.1672
2-N(NH_2)$\cdots Na^+$	-9.49	6.83	-47243.45	-90370.45	43127.00	47250.28	-16.33	0.1578	-39.43	-39.18	-5286.88	5247.70	-0.26	0.0043	3.97	4.08	-8640.30	8644.38	-0.11	0.0021	-44.95	-28.25	-16.70	0.1642

Table ST6: IQA components of complexes of the amino-substituted 1,2-azaborines with Na^+ calculated from the σ, π, and Na^+ parts of the total HF densities.

	σ		π		σ/π		cation		
Complexes	$E^{Ring\cdots Na^+}_{ne+C(\sigma)}$	$E^{Ring\cdots Na^+}_{XC(\sigma)}$	$E^{Ring\cdots Na^+}_{ne+C(\pi)}$	$E^{Ring\cdots Na^+}_{XC(\pi)}$	$E^{Ring\cdots Na^+}_{C(\sigma/\pi)}$	$E^{Ring\cdots Na^+}_{XC(\sigma/\pi)}$	$E^{Ring\cdots Na^+}_{ne+C(Na^+)}$	$E^{Ring\cdots Na^+}_{XC(Na^+)}$	$E^{Ring\cdots Na^+}_{en(CT)}$
2-B(NH_2)$\cdots Na^+$	-3617.79	-1.00	-704.48	-9.15	252.04	-1.14	-43146.05	-4.76	-46.56
2-C1(NH_2)$\cdots Na^+$	-3570.63	-1.00	-704.93	-9.31	252.07	-1.17	-43151.81	-4.83	-47.29
2-C2(NH_2)$\cdots Na^+$	-3579.13	-0.95	-700.85	-9.32	255.48	-1.19	-43152.06	-4.83	-47.23
2-C3(NH_2)$\cdots Na^+$	-3570.90	-1.01	-703.25	-9.35	260.40	-1.29	-43158.24	-4.85	-47.41
2-C4(NH_2)$\cdots Na^+$	-3586.51	-1.66	-671.06	-7.78	237.82	-2.16	-43157.53	-4.86	-47.55
2-N(NH_2)$\cdots Na^+$	-3591.37	-1.23	-699.28	-8.77	247.27	-1.47	-43152.06	-4.86	-47.51

Table ST7: IQA components of complexes of the nitro-substituted 1,2-azaborines with Na^+ calculated from the total (σ+π+Na^+) HF densities.

	Ring$\cdots Na^+$								$\sum$H$\cdots Na^+$						$NO_2\cdots Na^+$						Total			
Complexes	$E_{int}^{Ring\cdots Na^+}$	$E_{Cl}^{Ring\cdots Na^+}$	$E_{ne+C}^{Ring\cdots Na^+}$	$E_{en}^{Ring\cdots Na^+}$	$E_{C}^{Ring\cdots Na^+}$	$E_{nn}^{Ring\cdots Na^+}$	$E_{XC}^{Ring\cdots Na^+}$	δ(Ring, Na^+)	$\sum E_{int}^{H\cdots Na^+}$	$\sum E_{Cl}^{H\cdots Na^+}$	$\sum E_{ne+C}^{H\cdots Na^+}$	$\sum E_{nn}^{H\cdots Na^+}$	$\sum E_{XC}^{H\cdots Na^+}$	δ(H, Na^+)	$E_{int}^{NO_2\cdots Na^+}$	$E_{Cl}^{NO_2\cdots Na^+}$	$E_{ne+C}^{NO_2\cdots Na^+}$	$E_{nn}^{NO_2\cdots Na^+}$	$E_{XC}^{NO_2\cdots Na^+}$	δ(NO_2, Na^+)	E_{int}^{Tot}	E_{Cl}^{Tot}	E_{XC}^{Tot}	δ(aza, Na^+)
2-B(NO_2)$\cdots Na^+$	-42.01	-25.97	-47276.25	-90745.02	43468.77	47250.28	-16.04	0.1549	84.14	84.30	-5225.40	5309.70	-0.16	0.0027	-72.36	-72.25	-19811.47	19739.22	-0.11	0.0018	-30.23	-13.92	-16.31	0.1594
2-C1(NO_2)$\cdots Na^+$	7.36	23.06	-47227.23	-90184.41	42957.19	47250.28	-15.70	0.1511	12.43	12.64	-5251.65	5264.29	-0.21	0.0035	-47.63	-47.51	-20482.42	20434.91	-0.12	0.0023	-27.85	-11.81	-16.04	0.1569
2-C2(NO_2)$\cdots Na^+$	6.23	21.79	-47228.50	-90194.19	42965.69	47250.28	-15.56	0.1495	16.33	16.54	-5246.71	5263.24	-0.20	0.0033	-49.79	-49.64	-20454.15	20404.51	-0.15	0.0028	-27.22	-11.31	-15.91	0.1555
2-C3(NO_2)$\cdots Na^+$	1.84	17.41	-47232.87	-90247.51	43014.63	47250.28	-15.57	0.1495	15.79	15.99	-5252.37	5268.36	-0.20	0.0033	-46.03	-45.89	-20329.37	20283.49	-0.14	0.0026	-28.40	-12.48	-15.91	0.1554
2-C4(NO_2)$\cdots Na^+$	10.42	25.85	-47224.43	-90155.45	42931.02	47250.28	-15.43	0.1475	15.76	15.94	-5264.07	5280.00	-0.18	0.0029	-51.76	-51.57	-20183.79	20132.23	-0.19	0.0035	-25.58	-9.77	-15.80	0.1539
2-N(NO_2)$\cdots Na^+$	-8.31	7.46	-47242.82	-90350.86	43108.04	47250.28	-15.78	0.1521	-23.28	-23.05	-5270.75	5247.70	-0.23	0.0038	1.22	1.30	-20526.18	20527.48	-0.07	0.0014	-30.36	-14.29	-16.07	0.1574

Table ST8: IQA components of complexes of the nitro-substituted 1,2-azaborines with Na^+ calculated from the σ, π and Na^+ parts of the total HF densities.

	σ		π		σ/π		cation		
Complexes	$E^{Ring\cdots Na^+}_{ne+C(\sigma)}$	$E^{Ring\cdots Na^+}_{XC(\sigma)}$	$E^{Ring\cdots Na^+}_{ne+C(\pi)}$	$E^{Ring\cdots Na^+}_{XC(\pi)}$	$E^{Ring\cdots Na^+}_{C(\sigma/\pi)}$	$E^{Ring\cdots Na^+}_{XC(\sigma/\pi)}$	$E^{Ring\cdots Na^+}_{ne+C(Na^+)}$	$E^{Ring\cdots Na^+}_{XC(Na^+)}$	$E^{Ring\cdots Na^+}_{en(CT)}$
2-B(NO_2)$\cdots Na^+$	-3639.66	-0.93	-695.49	-9.12	249.88	-1.15	-43143.10	-4.84	-47.40
2-C1(NO_2)$\cdots Na^+$	-3594.69	-1.02	-692.58	-8.81	247.07	-1.14	-43140.26	-4.73	-46.26
2-C2(NO_2)$\cdots Na^+$	-3596.98	-0.91	-690.07	-8.74	243.30	-1.13	-43137.33	-4.78	-46.91
2-C3(NO_2)$\cdots Na^+$	-3597.70	-0.92	-695.02	-8.69	242.85	-1.13	-43135.17	-4.83	-47.34
2-C4(NO_2)$\cdots Na^+$	-3593.17	-0.93	-689.07	-8.59	238.82	-1.13	-43133.84	-4.77	-46.67
2-N(NO_2)$\cdots Na^+$	-3607.26	-1.01	-690.09	-8.82	242.57	-1.18	-43140.92	-4.76	-46.62

Table ST9: IQA components of complexes of the hydroxy-substituted 1,2-azaborines with Na^+ calculated from the total (σ+π+Na^+) HF densities.

	Ring$\cdots Na^+$								$\sum$H$\cdots Na^+$						X$\cdots Na^+$						Total			
Complexes	$E_{int}^{Ring\cdots Na^+}$	$E_{Cl}^{Ring\cdots Na^+}$	$E_{ne+C}^{Ring\cdots Na^+}$	$E_{en}^{Ring\cdots Na^+}$	$E_{C}^{Ring\cdots Na^+}$	$E_{nn}^{Ring\cdots Na^+}$	$E_{XC}^{Ring\cdots Na^+}$	δ(Ring, Na^+)	$\sum E_{int}^{H\cdots Na^+}$	$\sum E_{Cl}^{H\cdots Na^+}$	$\sum E_{ne+C}^{H\cdots Na^+}$	$\sum E_{nn}^{H\cdots Na^+}$	$\sum E_{XC}^{H\cdots Na^+}$	δ(H, Na^+)	$E_{int}^{OH\cdots Na^+}$	$E_{Cl}^{OH\cdots Na^+}$	$E_{ne+C}^{OH\cdots Na^+}$	$E_{nn}^{OH\cdots Na^+}$	$E_{XC}^{OH\cdots Na^+}$	δ(OH, Na^+)	E_{int}^{Tot}	E_{Cl}^{Tot}	E_{XC}^{Tot}	δ(aza, Na^+)
2-B(OH)$\cdots Na^+$	-31.18	-15.02	-47265.32	-90617.61	43352.29	47250.28	-16.15	0.1565	70.11	70.28	-5239.42	5309.70	-0.18	0.0031	-80.72	-80.62	-8770.80	8690.18	-0.10	0.0015	-41.80	-25.37	-16.43	0.1611
2-C1(OH)$\cdots Na^+$	26.65	42.83	-47207.46	-89948.46	42741.00	47250.28	-16.17	0.1565	-4.74	-4.50	-5268.78	5264.29	-0.25	0.0041	-62.97	-62.86	-8995.34	8932.48	-0.11	0.0017	-41.06	-24.53	-16.52	0.1623
2-C2(OH)$\cdots Na^+$	22.69	38.88	-47211.40	-89994.77	42783.37	47250.28	-16.19	0.1567	-0.56	-0.32	-5264.57	5263.24	-0.23	0.0038	-62.77	-62.64	-8980.16	8917.52	-0.14	0.0024	-40.64	-24.08	-16.56	0.1628
2-C3(OH)$\cdots Na^+$	23.61	39.91	-47210.37	-90001.18	42790.80	47250.28	-16.30	0.1574	-0.71	-0.48	-5268.84	5268.36	-0.24	0.0039	-62.62	-62.46	-8962.50	8900.04	-0.16	0.0029	-39.72	-23.03	-16.70	0.1641
2-C4(OH)$\cdots Na^+$	21.32	37.61	-47212.68	-90004.49	42791.81	47250.28	-16.29	0.1575	-0.50	-0.27	-5280.27	5280.00	-0.23	0.0037	-62.39	-62.22	-8856.96	8794.74	-0.17	0.0031	-41.58	-24.89	-16.69	0.1644
2-N(OH)$\cdots Na^+$	4.33	20.57	-47229.71	-90207.46	42977.75	47250.28	-16.23	0.1569	-34.12	-33.86	-5281.56	5247.70	-0.25	0.0042	-10.16	-10.08	-8881.24	8871.16	-0.09	0.0016	-39.95	-23.37	-16.57	0.1627

Table ST10: IQA components of complexes of the hydroxy-substituted 1,2-azaborines with Na^+ calculated from the σ, π, and Na^+ parts of the total HF densities.

	σ		π		σ/π		cation		
Complexes	$E^{Ring\cdots Na^+}_{ne+C(\sigma)}$	$E^{Ring\cdots Na^+}_{XC(\sigma)}$	$E^{Ring\cdots Na^+}_{ne+C(\pi)}$	$E^{Ring\cdots Na^+}_{XC(\pi)}$	$E^{Ring\cdots Na^+}_{C(\sigma/\pi)}$	$E^{Ring\cdots Na^+}_{XC(\sigma/\pi)}$	$E^{Ring\cdots Na^+}_{ne+C(Na^+)}$	$E^{Ring\cdots Na^+}_{XC(Na^+)}$	$E^{Ring\cdots Na^+}_{en(CT)}$
2-B(OH)$\cdots Na^+$	-3620.05	-1.00	-701.81	-9.21	250.54	-1.15	-43146.70	-4.78	-46.80
2-C1(OH)$\cdots Na^+$	-3561.30	-0.95	-699.05	-9.27	249.74	-1.15	-43149.31	-4.81	-47.05
2-C2(OH)$\cdots Na^+$	-3566.67	-0.97	-697.44	-9.23	250.33	-1.18	-43150.01	-4.81	-47.11
2-C3(OH)$\cdots Na^+$	-3564.80	-0.95	-699.67	-9.35	254.77	-1.17	-43152.94	-4.82	-47.23
2-C4(OH)$\cdots Na^+$	-3568.48	-0.94	-695.72	-9.24	251.98	-1.25	-43152.49	-4.85	-47.47
2-N(OH)$\cdots Na^+$	-3582.09	-0.94	-701.47	-9.21	251.02	-1.21	-43149.01	-4.87	-47.67

Table ST11: IQA components of complexes of benzene and its substituted derivatives with Na^+ calculated from the total (σ+π+Na^+) HF densities.

	Ring$\cdots Na^+$								$\sum$H$\cdots Na^+$						X$\cdots Na^+$						Total			
Complexes	$E_{int}^{Ring\cdots Na^+}$	$E_{Cl}^{Ring\cdots Na^+}$	$E_{ne+C}^{Ring\cdots Na^+}$	$E_{en}^{Ring\cdots Na^+}$	$E_{C}^{Ring\cdots Na^+}$	$E_{nn}^{Ring\cdots Na^+}$	$E_{XC}^{Ring\cdots Na^+}$	δ(Ring, Na^+)	$\sum E_{int}^{H\cdots Na^+}$	$\sum E_{Cl}^{H\cdots Na^+}$	$\sum E_{ne+C}^{H\cdots Na^+}$	$\sum E_{nn}^{H\cdots Na^+}$	$\sum E_{XC}^{H\cdots Na^+}$	δ(H, Na^+)	$E_{int}^{X\cdots Na^+}$	$E_{Cl}^{X\cdots Na^+}$	$E_{ne+C}^{X\cdots Na^+}$	$E_{nn}^{X\cdots Na^+}$	$E_{XC}^{X\cdots Na^+}$	δ(X, Na^+)	E_{int}^{Tot}	E_{Cl}^{Tot}	E_{XC}^{Tot}	δ(aza, Na^+)
Benzene$\cdots Na^+$	-87.22	-70.26	-47405.12	-91434.61	44029.49	47334.86	-16.96	0.1641	40.92	41.14	-6259.29	6300.42	-0.21	0.0037							-46.30	-29.13	-17.17	0.1678
Benzene$\cdots Na^+$(2.5 Å)	-78.80	-64.89	-45847.95	-88398.74	42550.78	45783.07	-13.92	0.1405	38.40	38.58	-6125.61	6164.19	-0.18	0.0032							-40.40	-26.30	-14.10	0.1438
Ben-F$\cdots Na^+$	-12.41	4.37	-47330.48	-90560.06	43229.58	47334.86	-16.78	0.1610	42.07	42.24	-5208.14	5250.37	-0.17	0.0029	-69.95	-69.84	-9030.50	8960.66	-0.11	0.0020	-40.30	-23.23	-17.07	0.1659
Ben-CN$\cdots Na^+$	-60.99	-44.66	-47379.48	-91124.46	43744.97	47334.86	-16.36	0.1569	44.53	44.69	-5202.99	5247.68	-0.16	0.0028	-18.35	-18.22	-11298.36	11280.13	-0.12	0.0023	-34.80	-18.16	-16.64	0.1620
Ben-NH2$\cdots Na^+$	-26.66	-9.61	-47344.47	-90731.83	43387.35	47334.86	-17.04	0.1641	28.96	29.15	-5222.02	5251.16	-0.19	0.0033	-52.33	-52.19	-8682.21	8630.02	-0.15	0.0027	-50.04	-32.66	-17.38	0.1701
Ben-NO2$\cdots Na^+$(2.5 Å)	-30.22	-16.85	-45799.92	-87856.85	42056.93	45783.07	-13.36	0.1335	50.63	50.75	-5085.45	5136.20	-0.12	0.0022	-45.96	-45.85	-19840.24	19794.40	-0.11	0.0020	-25.55	-11.95	-13.60	0.1378
Ben-OH$\cdots Na^+$	-15.67	1.26	-47333.60	-90601.39	43267.79	47334.86	-16.93	0.1629	34.53	34.71	-5215.66	5250.37	-0.18	0.0031	-63.72	-63.56	-8893.99	8830.40	-0.13	0.0024	-44.87	-27.62	-17.25	0.1684

Table ST12: IQA components of complexes of benzene and its substituted derivatives with Na^+ from the σ, π, and Na^+ parts of the total HF densities.

	σ		π		σ/π		cation		
Complexes	$E^{Ring\cdots Na^+}_{ne+C(\sigma)}$	$E^{Ring\cdots Na^+}_{XC(\sigma)}$	$E^{Ring\cdots Na^+}_{ne+C(\pi)}$	$E^{Ring\cdots Na^+}_{XC(\pi)}$	$E^{Ring\cdots Na^+}_{C(\sigma/\pi)}$	$E^{Ring\cdots Na^+}_{XC(\sigma/\pi)}$	$E^{Ring\cdots Na^+}_{ne+C(cation)}$	$E^{Ring\cdots Na^+}_{XC(Na^+)}$	$E^{Ring\cdots Na^+}_{en(CT)}$
Benzene$\cdots Na^+$	-3698.46	-0.88	-695.54	-9.91	269.54	-1.18	-43231.35	-4.99	-48.81
Benzene$\cdots Na^+$(2.5 Å)	-3568.85	-0.67	-676.89	-8.51	230.75	-0.90	-41794.83	-3.84	-37.65
Ben-F$\cdots Na^+$	-3614.69	-0.86	-700.11	-9.71	260.69	-1.17	-43226.52	-5.05	-49.32
Ben-CN$\cdots Na^+$	-3672.03	-0.85	-695.24	-9.41	258.09	-1.15	-43221.33	-4.96	-48.49
Ben-NH2$\cdots Na^+$	-3621.65	-0.87	-706.75	-9.96	268.78	-1.18	-43235.14	-5.04	-49.21
Ben-NO2$\cdots Na^+$(2.5 Å)	-3522.77	-0.62	-678.48	-8.00	223.60	-0.88	-41783.84	-3.86	-37.95
Ben-OH$\cdots Na^+$	-3608.09	-1.19	-698.27	-9.06	254.11	-1.63	-43231.43	-5.06	-49.42