Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting information

Is π halogen bonding or lone pair···π interaction formed between borazine and some halogenated compounds?

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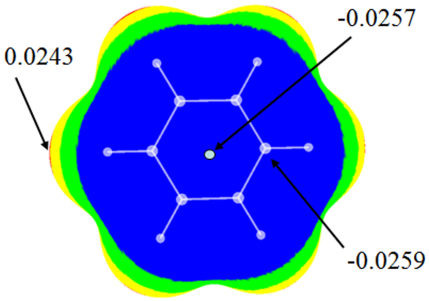

Fig. S1. Molecular electrostatic potentials of benzene. Color ranges, in eV, are: red, greater than 0.02; yellow, between 0.02 and 0.01; green, between 0.01 and 0; blue, less than 0

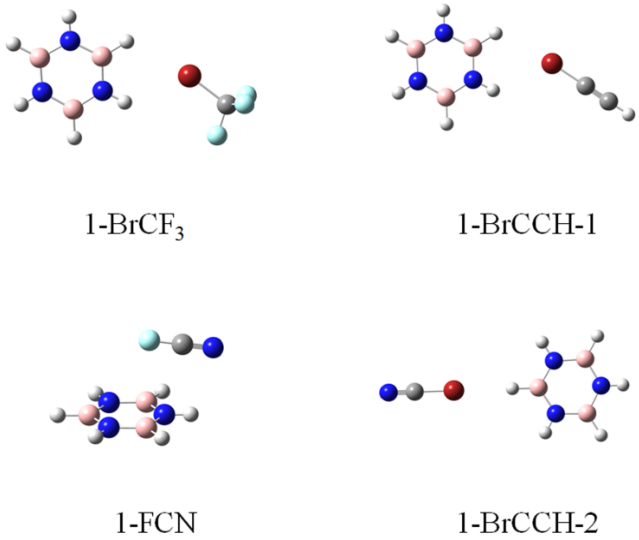

Fig. S2 Other possible structures between **1** and halogenated molecules

In Figure S2, other possible structures between **1** and halogenated molecules are shown. The halogen atom in **1**-$BrCF_3$ and **1**-BrCCH-1 complexes acts as the Lewis base to form a hydrogen bond with the hydrogen on NH group and as the Lewis acid to form

a halogen-hydride halogen bond with the hydrogen on BH group simultaneously. For **1**-BrCCH-2 complex, only a halogen-hydride halogen bond is present and its interaction energy is about -5 kJ/mol. For **1**-FCN complex, three interactions are possible: the N···H interaction between the H atom in **1** and the N atom in FCN, the C···N interaction between the N atom in **1** and the C atom in FCN, and the F···π interaction between the electron-deficient π center in **1** and the F atom in FCN. Even so, its interaction energy is -8.57 kJ/mol. Clearly, it is more stable than **1**-FCN-a complex.

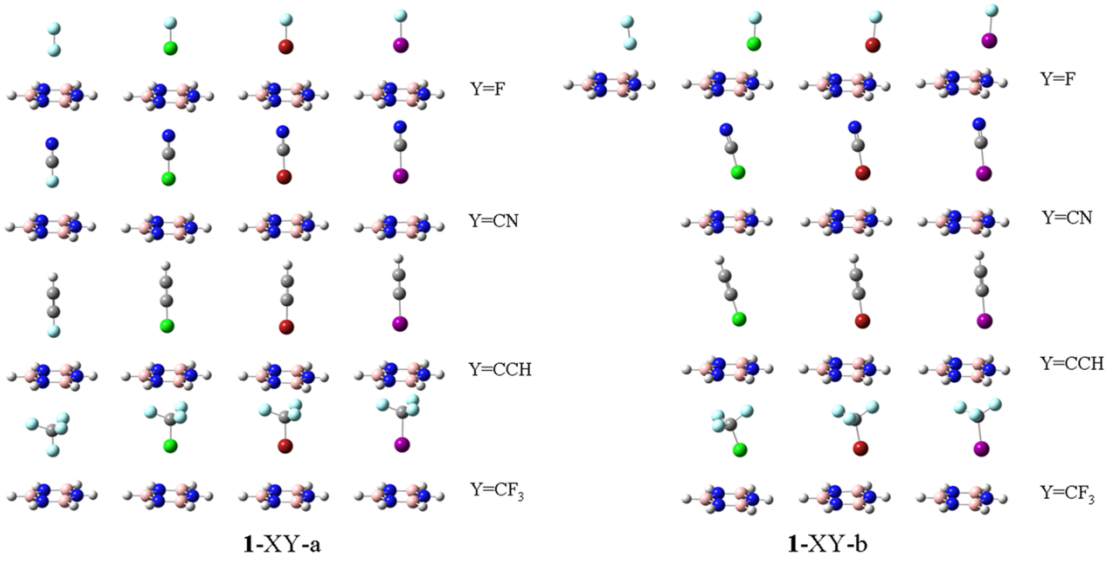

Fig. S3 Optimized structures of **1**-XY (X = F, Cl, Br, and I) complexes

Table S1 The SAPT analysis of the interaction energy of the a type complexes. All values are given in kJ/mol.

	1-FF-a	**1**-ClF-a	**1**-BrF-a	**1**-FCN-a	**1**-ClCN-a	**1**-BrCN-a	**1**-FCCH-a	**1**-ClCCH-a	**1**-BrCCH-a	**1**-FCF_3-a	**1**-$ClCF_3$-a	**1**-$BrCF_3$-a
$E_{elst}^{(10)}$	5.55	-11.21	-17.99	-6.98	-8.28	-14.22	-0.65	-5.85	-11.23	-1.69	-6.93	-12.06
$E_{elst,resp}^{(12)}$	-0.54	-0.80	-1.48	-0.90	-1.00	-1.53	-0.90	-1.21	-1.78	-0.71	-0.86	-1.32
E_{elst}	5.01	-12.01	-19.47	-7.88	-9.28	-15.75	-1.55	-7.06	-13.01	-2.40	-7.79	-13.38
$E_{exch}^{(10)}$	9.16	14.54	22.63	25.74	13.66	21.10	7.31	12.64	19.80	7.39	11.85	18.05
$E_{exch}^{(11)}$	-0.28	0.10	0.38	0.14	0.00	0.35	-0.31	-0.01	0.34	-0.27	0.05	0.38
$E_{exch}^{(12)}$	1.97	2.20	3.11	1.88	1.96	2.66	1.80	1.93	2.56	1.66	1.69	2.30
E_{exch}	10.85	16.84	26.12	27.76	15.62	24.11	8.80	14.56	22.70	8.78	13.59	20.73
$E_{ind,resp}^{(20)}$	-6.79	-9.43	-21.43	-6.86	-6.7.0	-16.00	-2.18	-5.28	-13.07	-2.22	-5.45	-13.00
$E_{ex-ind,r}^{(20)}$	2.07	7.08	15.83	6.23	5.63	13.01	2.00	4.86	11.40	2.25	4.70	10.69
$tE_{ind}^{(22)}$	-0.84	-1.35	-3.35	-1.25	-1.45	-3.24	-0.54	-1.37	-3.05	-0.62	-1.23	-2.70
$tE_{ex-ind^*}^{(22)}$	0.25	1.02	2.47	1.13	1.22	2.64	0.51	1.25	2.67	0.63	1.06	2.21
E_{ind}	-5.31	-2.68	-6.48	-0.75	-1.30	-3.59	-0.21	-0.54	-2.05	0.04	-0.92	-2.80
$E_{disp}^{(20)}$	-3.69	-9.85	-14.36	-15.49	-10.86	-15.52	-5.60	-10.67	-15.25	-5.02	-9.87	-14.12
$E_{exch-disp}^{(20)}$	0.60	0.91	1.45	2.28	1.00	1.56	0.46	1.01	1.62	0.42	0.88	1.37
E_{disp}	-3.09	-8.94	-12.91	-13.21	-9.86	-13.96	-5.14	-9.66	-13.63	-4.60	-8.99	-12.75
$\delta E_{\mathrm{int},r}^{HF}$	-0.35	-1.92	-3.93	-1.59	-0.96	-2.19	-0.38	-0.74	-1.65	-0.36	-0.81	-1.88
E_{int}^{SAPT0}	6.91	-7.96	-13.88	4.90	-5.55	-10.04	1.33	-3.30	-6.73	1.11	-4.83	-9.08
E_{int}^{SAPT2}	7.11	-8.71	-16.67	4.33	-5.78	-11.38	1.52	-3.44	-7.64	1.46	-4.92	-10.08

Table S2 The SAPT analysis of the interaction energy of the b type complexes. All values are given in kJ/mol.

	1-FF-b	**1**-ClF-b	**1**-BrF-b	**1**-ClCN-b	**1**-BrCN-b	**1**-ClCCH-b	**1**-BrCCH-b	**1**-ClCF$_3$-b	**1**-BrCF$_3$-b
$E_{elst}^{(10)}$	-21.26	-62.71	-106.03	-11.01	-23.63	-8.44	-19.11	-9.21	-18.70
$E_{elst,resp}^{(12)}$	-3.36	0.81	0.99	-0.99	-1.20	-1.26	-1.66	-0.91	-1.20
E_{elst}	-24.62	-61.90	-105.04	-12.00	-24.83	-9.70	-20.77	-10.12	-19.90
$E_{exch}^{(10)}$	40.42	92.15	140.72	17.72	32.09	16.82	29.25	15.81	26.30
$E_{exch}^{(11)}$	0.13	0.62	0.82	0.02	0.50	0.01	0.47	0.08	0.54
$E_{exch}^{(12)}$	6.14	8.38	13.39	2.39	3.76	2.41	3.56	2.11	3.20
E_{exch}	46.69	101.15	154.93	20.13	36.35	19.24	33.28	18.00	30.04
$E_{ind,resp}^{(20)}$	-11.18	-114.59	-293.51	-11.07	-38.54	-9.28	-31.14	-8.91	-28.23
$E_{ex-ind,r}^{(20)}$	7.53	99.34	252.08	9.70	33.50	8.60	28.01	7.94	24.51
$tE_{ind}^{(22)}$	-1.89	-11.05	-30.74	-2.12	-6.52	-2.05	-5.91	-1.80	-5.06
$tE_{ex-ind^*}^{(22)}$	1.28	9.58	26.4	1.86	5.67	1.89	5.32	1.60	4.39
E_{ind}	-4.26	-16.72	-45.77	-1.63	-5.89	-0.84	-3.72	-1.17	-4.39
$E_{disp}^{(20)}$	-10.11	-25.6	-36.98	-12.13	-18.27	-12.07	-17.87	-11.22	-16.46
$E_{exch-disp}^{(20)}$	1.88	4.74	6.93	1.30	2.22	1.37	2.28	1.19	1.91
E_{disp}	-8.23	-20.86	-30.05	-10.83	-16.05	-10.70	-15.59	-10.03	-14.55
$\delta E_{\mathrm{int},r}^{HF}$	-0.98	-24.48	-34.37	-1.52	-4.39	-1.21	-3.23	-1.31	-3.71
E_{int}^{SAPT0}	7.27	-6.65	-36.81	-5.47	-12.63	-2.99	-8.95	-4.40	-10.70
E_{int}^{SAPT2}	8.60	-22.81	-60.30	-5.85	-14.81	-3.21	-10.03	-4.63	-12.51

In Tables S1 and S2, the following formulas have been used to calculate the components of the interaction energies.

$$E_{elst} = E_{elst}^{(10)} + E_{elst}^{(12)}$$

$$E_{exch} = E_{exch}^{(10)} + E_{exch}^{(11)} + E_{exch}^{(12)}$$

$$E_{ind} = E_{ind,resp}^{(20)} + E_{ex-ind,r}^{(20)} + tE_{ind}^{(22)} + tE_{ex-ind^*}^{(22)}$$

$$E_{disp} = E_{disp}^{(20)} + E_{exch-disp}^{(20)}$$

$$E_{\mathrm{int}}^{SAPT0} = E_{elst}^{(10)} + E_{exch}^{(10)} + E_{ind,resp}^{(20)} + E_{ex-ind,r}^{(20)} + E_{disp}^{(20)} + E_{exch-disp}^{(20)}$$

$$E_{\mathrm{int}}^{SAPT2} = E_{\mathrm{int}}^{SAPT0} + E_{elst}^{(12)} + E_{exch}^{(11)} + E_{exch}^{(12)} + tE_{ind}^{(22)} + tE_{ex-ind^*}^{(22)} + \delta E_{\mathrm{int},r}^{HF}$$

$$\delta E_{\mathrm{int},r}^{HF} = E_{\mathrm{int}}^{HF} - E_{elst}^{(10)} - E_{exch}^{(10)} - E_{ind,resp}^{(20)} - E_{ex-ind,r}^{(20)}$$