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

What kind of neutral halogen bonds can be modulated by solvent effects?

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Table S1. The differences of electron density, its Laplacian and the |V/G| values by ωB97X-D/ACCD.

	ε=1			ε=2.27			ε=4.18			ε=7.22			ε=78.36		
	ρ	∇^2_ρ	|V/G|	ρ	∇^2_ρ	|V/G|	ρ	∇^2_ρ	|V/G|	ρ	∇^2_ρ	|V/G|	ρ	∇^2_ρ	|V/G|
BrF…pyridine	0.067	0.149	1.232	0.083	0.149	1.367	0.092	0.146	1.437	0.097	0.143	1.481	0.105	0.136	1.536
ClF…pyridine	0.072	0.166	1.200	0.106	0.141	1.502	0.124	0.106	1.666	0.137	0.072	1.791	0.153	0.020	1.944
I_2…pyridine	0.038	0.091	1.087	0.045	0.102	1.150	0.050	0.108	1.186	0.053	0.112	1.211	0.057	0.116	1.245
Br_2…pyridine	0.041	0.112	1.014	0.054	0.129	1.119	0.072	0.141	1.274	0.073	0.139	1.292	0.092	0.133	1.456
Cl_2…pyridine	0.035	0.112	0.914	0.049	0.139	1.005	0.063	0.156	1.123	0.154	0.016	1.956	0.185	-0.114	2.279
BrF…NH_3	0.053	0.132	1.115	0.070	0.141	1.271	0.078	0.140	1.344	0.084	0.137	1.396	0.093	0.133	1.471
ClF…NH_3	0.053	0.147	1.045	0.079	0.155	1.276	0.098	0.138	1.457	0.110	0.118	1.569	0.129	0.074	1.761
I_2…NH_3	0.031	0.078	1.016	0.039	0.093	1.090	0.044	0.100	1.134	0.048	0.105	1.168	0.054	0.111	1.216
Br_2…NH_3	0.033	0.096	0.940	0.044	0.115	1.027	0.059	0.133	1.160	0.061	0.131	1.178	0.077	0.133	1.328
Cl_2…NH_3	0.030	0.097	0.872	0.039	0.119	0.928	0.049	0.137	0.999	0.061	0.150	1.102	0.147	0.020	1.939
BrF…H_2S	0.033	0.080	0.995	0.042	0.086	1.105	0.047	0.087	1.182	0.052	0.086	1.244	0.057	0.156	1.131
ClF…H_2S	0.030	0.083	0.914	0.040	0.094	1.015	0.055	0.100	1.201	0.057	0.098	1.222	0.056	0.172	1.049
I_2…H_2S	0.019	0.058	0.946	0.022	0.066	0.967	0.023	0.068	0.976	0.023	0.070	0.981	0.030	0.083	1.042
Br_2…H_2S	0.018	0.049	0.819	0.020	0.055	0.842	0.022	0.058	0.855	0.022	0.058	0.857	0.031	0.095	0.967
Cl_2…H_2S	0.016	0.048	0.785	0.018	0.053	0.795	0.018	0.055	0.800	0.019	0.056	0.803	0.027	0.093	0.913
BrF…Me_2O	0.041	0.127	1.032	0.048	0.140	1.074	0.052	0.146	1.095	0.054	0.150	1.110	0.045	0.142	1.028
ClF…Me_2O	0.038	0.132	0.960	0.045	0.149	0.991	0.052	0.164	1.026	0.052	0.164	1.026	0.031	0.118	0.880
I_2…Me_2O	0.025	0.071	1.006	0.027	0.075	1.020	0.028	0.078	1.028	0.029	0.080	1.034	0.020	0.063	0.917
Br_2…Me_2O	0.025	0.081	0.943	0.028	0.088	0.955	0.029	0.091	0.960	0.030	0.093	0.963	0.018	0.065	0.834
Cl_2…Me_2O	0.023	0.082	0.904	0.025	0.086	0.908	0.026	0.090	0.910	0.026	0.090	0.911	0.015	0.059	0.798
BrF…H_2O	0.031	0.104	0.969	0.038	0.121	1.002	0.040	0.127	1.017	0.042	0.131	1.029	0.045	0.137	1.045
ClF…H_2O	0.028	0.102	0.913	0.034	0.120	0.932	0.036	0.126	0.940	0.037	0.128	0.944	0.039	0.135	0.955
I_2…H_2O	0.019	0.058	0.946	0.022	0.066	0.967	0.023	0.068	0.976	0.023	0.070	0.981	0.024	0.072	0.989
Br_2…H_2O	0.019	0.066	0.897	0.021	0.072	0.908	0.022	0.074	0.913	0.023	0.076	0.916	0.023	0.078	0.920
Cl_2…H_2O	0.017	0.064	0.871	0.019	0.070	0.876	0.020	0.072	0.879	0.020	0.073	0.880	0.020	0.074	0.882
BrF…HCN	0.029	0.105	0.908	0.036	0.122	0.956	0.039	0.129	0.980	0.041	0.134	0.998	0.059	0.082	1.336
ClF…HCN	0.023	0.091	0.832	0.027	0.104	0.852	0.028	0.108	0.861	0.029	0.111	0.867	0.073	0.084	1.441
I_2…HCN	0.017	0.054	0.887	0.019	0.059	0.904	0.020	0.060	0.910	0.020	0.061	0.913	0.022	0.052	0.939
Br_2…HCN	0.016	0.058	0.818	0.017	0.061	0.827	0.018	0.063	0.830	0.018	0.064	0.832	0.023	0.060	0.867
Cl_2…HCN	0.014	0.052	0.788	0.015	0.057	0.794	0.015	0.057	0.796	0.015	0.058	0.797	0.020	0.058	0.808

Table S2. The geometrical parameters of halogen bonds in various environments by M06-2X/ACCD.

		ε = 1.0		ε =2.27		ε =4.18		ε = 7.22		ε = 78.36	
XB donor	XB acceptor	*R* (Å)	∠YXR (°)	*R* (Å)	∠YXR (°)	*R* (Å)	∠YXR (°)	*R* (Å)	∠YXR (°)	*R* (Å)	∠YXR (°)
BrF	pyridine	2.240	180.00	2.158	179.97	2.123	179.95	2.100	179.97	2.073	179.97
ClF	pyridine	2.179	179.97	2.048	180.00	1.989	180.00	1.949	180.00	1.895	179.97
I_2	pyridine	2.580	179.95	2.476	180.00	2.433	179.97	2.403	179.95	2.364	180.00
Br_2	pyridine	2.429	179.95	2.282	180.00	2.213	180.00	2.170	180.00	2.099	179.95
Cl_2	pyridine	2.526	179.88	2.325	180.00	2.123	179.96	1.975	180.00	1.780	179.94
BrF	NH_3	2.350	179.97	2.231	180.00	2.186	180.00	2.158	179.97	2.121	180.00
ClF	NH_3	2.327	179.88	2.148	179.96	2.042	179.96	2.036	179.96	1.970	179.97
I_2	NH_3	2.702	179.88	2.548	179.90	2.486	179.91	2.447	179.87	2.394	179.84
Br_2	NH_3	2.577	179.90	2.387	179.95	2.248	179.93	2.240	179.94	2.160	179.97
Cl_2	NH_3	2.629	179.84	2.485	180.00	2.289	179.92	2.144	179.95	1.951	179.96
BrF	H_2S	2.854	179.96	2.697	179.77	2.639	179.66	2.605	179.55	2.558	179.43
ClF	H_2S	2.895	179.26	2.762	179.83	2.576	179.71	2.565	179.69	2.470	179.57
I_2	H_2S	3.272	178.20	3.200	179.43	3.163	179.84	3.130	179.94	3.074	179.77
Br_2	H_2S	3.129	177.89	3.057	178.89	2.982	179.82	2.975	179.86	2.909	179.87
Cl_2	H_2S	3.116	178.33	3.077	179.49	3.066	179.09	3.056	179.25	3.041	179.22
BrF	Me_2O	2.424	178.02	2.340	178.89	2.306	179.17	2.285	179.33	2.258	179.52
ClF	Me_2O	2.430	177.22	2.365	178.14	2.310	178.69	2.307	178.72	2.269	179.02
I_2	Me_2O	2.746	176.74	2.701	177.85	2.678	178.28	2.663	178.54	2.644	178.83
Br_2	Me_2O	2.648	175.79	2.611	177.06	2.592	177.52	2.583	177.78	2.568	178.05
Cl_2	Me_2O	2.628	174.65	2.607	176.04	2.594	176.80	2.593	176.84	2.586	177.19
BrF	H_2O	2.563	179.91	2.495	179.28	2.461	179.07	2.437	178.95	2.404	178.82
ClF	H_2O	2.551	179.04	2.505	179.89	2.484	179.65	2.471	179.45	2.452	179.26
I_2	H_2O	2.862	178.95	2.811	179.92	2.789	179.49	2.774	179.25	2.757	178.95
Br_2	H_2O	2.766	178.53	2.728	179.83	2.713	179.79	2.703	179.53	2.692	179.26
Cl_2	H_2O	2.727	178.48	2.704	179.57	2.696	179.97	2.690	179.72	2.684	179.42
BrF	HCN	2.638	179.94	2.567	179.94	2.534	179.87	2.512	179.96	2.477	179.92
ClF	HCN	2.653	180.00	2.612	180.00	2.595	180.00	2.584	180.00	2.571	179.96
I_2	HCN	2.959	180.00	2.918	179.97	2.902	179.97	2.892	180.00	2.880	180.00
Br_2	HCN	2.874	180.00	2.845	180.00	2.834	179.97	2.827	180.00	2.820	180.00
Cl_2	HCN	2.846	180.00	2.827	179.97	2.820	180.00	2.816	180.00	2.812	179.97

Table S3. GKS-EDA results for XB dimers in gas phase based on M06-2X/ACCD. (kcal/mol)

XB donor	XB acceptor	ΔE^{ele}	ΔE^{Pauli}	ΔE^{pol}	$\Delta E^{corr+disp}$	ΔE^{int}
BrF	pyridine	-50.45	78.43	-36.33	-10.09	-18.44
ClF	pyridine	-41.64	70.91	-33.25	-11.43	-15.42
I_2	pyridine	-28.56	45.79	-19.06	-9.13	-10.96
Br_2	pyridine	-30.10	49.03	-18.24	-9.39	-8.70
Cl_2	pyridine	-15.78	25.16	-8.95	-6.48	-6.06
BrF	NH_3	-40.28	58.52	-26.87	-6.83	-15.46
ClF	NH_3	-29.87	46.44	-21.15	-7.87	-12.46
I_2	NH_3	-22.90	33.69	-14.06	-7.16	-10.43
Br_2	NH_3	-21.97	32.82	-12.26	-6.34	-7.75
Cl_2	NH_3	-13.19	19.51	-7.11	-5.13	-5.91
BrF	H_2S	-17.31	28.71	-12.97	-6.99	-8.56
ClF	H_2S	-10.91	18.49	-7.72	-6.14	-6.28
I_2	H_2S	-8.94	15.01	-5.83	-5.32	-5.08
Br_2	H_2S	-8.77	14.66	-4.87	-5.63	-4.61
Cl_2	H_2S	-6.12	10.60	-3.29	-4.61	-3.42
BrF	Me_2O	-21.53	30.03	-12.62	-6.25	-10.37
ClF	Me_2O	-14.71	21.22	-8.29	-6.56	-8.34
I_2	Me_2O	-13.81	19.86	-6.48	-8.71	-9.13
Br_2	Me_2O	-11.81	17.14	-5.02	-6.25	-5.93
Cl_2	Me_2O	-8.39	12.53	-3.37	-5.97	-5.19
BrF	H_2O	-14.18	17.15	-7.56	-2.99	-7.58
ClF	H_2O	-10.30	12.92	-5.21	-3.90	-6.49
I_2	H_2O	-9.60	12.07	-4.31	-2.61	-4.45
Br_2	H_2O	-8.15	10.40	-3.32	-3.19	-4.27
Cl_2	H_2O	-6.14	8.04	-2.47	-2.91	-3.48
BrF	HCN	-11.45	14.70	-6.96	-3.47	-7.17
ClF	HCN	-7.69	9.88	-4.24	-3.13	-5.18
I_2	HCN	-7.53	10.38	-4.06	-3.37	-4.58
Br_2	HCN	-5.98	8.11	-2.83	-2.95	-3.65
Cl_2	HCN	-4.35	5.93	-1.95	-2.41	-2.78

Table S4. The bond distance difference (ΔR, Å) and the binding energy difference ($\Delta\Delta G^{int}$, kcal/mol) by GKS-EDA in various solutions by ωB97X-D/ACCD.

		ε=2.27		ε=4.18		ε=7.22		ε=78.36	
		ΔR	$\Delta\Delta G^{int}$	ΔR	$\Delta\Delta G^{int}$	ΔR	$\Delta\Delta G^{int}$	ΔR	$\Delta\Delta G^{int}$
Type A	BrF…pyridine	-0.09	-6.53	-0.13	-10.44	-0.16	-13.34	-0.19	-17.49
	ClF…pyridine	-0.16	-9.95	-0.22	-16.78	-0.26	-22.89	-0.31	-32.01
	I_2…pyridine	-0.09	-1.82	-0.13	-2.87	-0.16	-3.68	-0.20	-4.96
	Br_2…pyridine	-0.12	-2.55	-0.20	-4.80	-0.26	-6.99	-0.36	-12.52
	Cl_2…pyridine	-0.14	-2.11	-0.26	-4.63	-0.64	-31.03	-0.72	-52.80
	BrF…NH_3	-0.12	-5.38	-0.17	-8.46	-0.20	-10.83	-0.25	-14.48
	ClF…NH_3	-0.17	-7.44	-0.25	-13.31	-0.30	-17.81	-0.37	-26.49
	I_2…NH_3	-0.13	-2.30	-0.19	-3.66	-0.23	-4.71	-0.28	-6.37
	Br_2…NH_3	-0.13	-2.51	-0.26	-5.08	-0.27	-6.13	-0.38	-10.03
	Cl_2…NH_3	-0.12	-1.93	-0.22	-3.68	-0.32	-27.56	-0.69	-31.54
	BrF…H_2S	-0.11	-2.98	-0.17	-4.89	-0.21	-6.42	-0.26	-8.90
	ClF…H_2S	-0.12	-2.41	-0.27	-5.66	-0.28	-6.59	-0.39	-11.64
	BrF…Me_2O	-0.07	-2.02	-0.10	-3.06	-0.12	-3.79	-0.14	-4.79
	ClF…Me_2O	-0.07	-1.51	-0.12	-2.57	-0.13	-2.93	-0.16	-3.83
	BrF…H_2O	-0.08	-1.21	-0.11	-1.80	-0.13	-2.20	-0.16	-2.81
	ClF…H_2O	-0.08	-0.64	-0.11	-0.93	-0.12	-1.13	-0.14	-1.41
	BrF…HCN	-0.06	-1.53	-0.08	-2.29	-0.10	-2.79	-0.13	-3.49
	ClF…HCN	-0.09	-1.04	-0.12	-1.53	-0.15	-1.83	-0.19	-2.30
Type B	I_2…H_2S	-0.07	-0.54	-0.11	-0.79	-0.14	-0.97	-0.18	-1.20
	Br_2…H_2S	-0.08	-0.53	-0.11	-0.80	-0.11	-0.92	-0.13	-1.15
	Cl_2…H_2S	-0.06	-0.34	-0.08	-0.49	-0.09	-0.58	-0.11	-0.71
	I_2…Me_2O	-0.04	-0.43	-0.06	-0.60	-0.07	-0.71	-0.09	-0.84
	Br_2…Me_2O	-0.05	-0.31	-0.07	-0.46	-0.08	-0.56	-0.09	-0.69
	Cl_2…Me_2O	-0.03	-0.25	-0.05	-0.39	-0.05	-0.44	-0.07	-0.53
	I_2…H_2O	-0.07	-0.25	-0.09	-0.37	-0.11	-0.43	-0.12	-0.52
	Br_2…H_2O	-0.05	-0.15	-0.06	-0.22	-0.08	-0.26	-0.09	-0.32
	Cl_2…H_2O	-0.05	-0.04	-0.06	-0.06	-0.07	-0.07	-0.08	-0.09
	I_2…HCN	-0.05	-0.37	-0.06	-0.55	-0.07	-0.67	-0.08	-0.83
	Br_2…HCN	-0.03	-0.36	-0.04	-0.51	-0.05	-0.61	-0.05	-0.73
	Cl_2…HCN	-0.04	-0.23	-0.04	-0.32	-0.05	-0.38	-0.05	-0.45

Table S5. The GKS-EDA results with ε=2.27 calculated at ωB97X-D/ACCD. (kcal/mol)

XB donor	XB acceptor	ΔG^{ele}	ΔG^{Pauli}	ΔG^{pol}	ΔG^{desol}	$\Delta G^{corr+disp}$	ΔG^{int}
BrF	pyridine	-65.17	102.16	-46.65	-4.46	-11.99	-26.11
ClF	pyridine	-69.30	124.37	-61.46	-5.19	-15.54	-27.12
I_2	pyridine	-32.55	52.06	-20.70	-1.60	-9.96	-12.75
Br_2	pyridine	-36.33	59.53	-21.45	-1.83	-11.38	-11.45
Cl_2	pyridine	-25.98	44.90	-15.02	-1.32	-11.44	-8.85
BrF	NH_3	-56.84	85.43	-37.29	-4.20	-8.99	-21.87
ClF	NH_3	-51.86	88.19	-40.28	-5.07	-12.50	-21.51
I_2	NH_3	-29.60	45.27	-17.42	-2.36	-8.44	-12.57
Br_2	NH_3	-30.79	48.02	-16.56	-2.28	-8.90	-10.51
Cl_2	NH_3	-21.79	35.56	-11.32	-1.59	-9.04	-8.18
BrF	H_2S	-25.57	44.92	-19.57	-2.36	-9.53	-12.11
ClF	H_2S	-19.84	37.80	-15.11	-1.63	-10.51	-9.30
I_2	H_2S	-9.72	16.42	-6.16	-0.46	-5.36	-5.26
Br_2	H_2S	-10.19	17.47	-5.61	-0.45	-5.90	-4.67
Cl_2	H_2S	-6.99	12.41	-3.48	-0.27	-4.93	-3.25
BrF	Me_2O	-27.03	38.92	-15.14	-1.55	-7.72	-12.52
ClF	Me_2O	-20.33	31.43	-11.02	-1.07	-8.83	-9.82
I_2	Me_2O	-14.12	19.85	-6.24	-0.36	-8.72	-9.59
Br_2	Me_2O	-12.87	18.52	-4.99	-0.29	-5.83	-5.46
Cl_2	Me_2O	-8.97	13.26	-3.12	-0.16	-5.75	-4.73
BrF	H_2O	-18.24	26.47	-9.72	-1.47	-5.84	-8.51
ClF	H_2O	-10.81	15.19	-4.86	-0.94	-4.45	-5.52
I_2	H_2O	-8.93	12.34	-3.87	-0.48	-3.75	-4.53
Br_2	H_2O	-6.99	9.40	-2.50	-0.38	-3.22	-3.47
Cl_2	H_2O	-4.79	6.34	-1.53	-0.24	-2.34	-2.36
BrF	HCN	-20.15	27.16	-9.54	-1.18	-4.90	-8.89
ClF	HCN	-14.48	20.53	-6.45	-0.60	-5.81	-7.15
I_2	HCN	-11.07	14.27	-3.99	-0.32	-2.01	-3.27
Br_2	HCN	-9.41	12.32	-3.04	-0.17	-3.22	-3.72
Cl_2	HCN	-6.80	9.10	-2.04	-0.05	-2.91	-2.89

Table S6. The GKS-EDA results with ε=4.18 calculated at ωB97X-D/ACCD. (kcal/mol)

XB donor	XB acceptor	ΔG^{ele}	ΔG^{Pauli}	ΔG^{pol}	ΔG^{desol}	$\Delta G^{corr+disp}$	ΔG^{int}
BrF	pyridine	-74.06	117.53	-53.50	-7.18	-12.81	-30.02
ClF	pyridine	-84.02	153.47	-78.35	-9.07	-15.98	-33.95
I_2	pyridine	-36.85	60.19	-23.70	-2.63	-10.80	-13.80
Br_2	pyridine	-45.93	77.46	-28.54	-3.48	-13.21	-13.70
Cl_2	pyridine	-36.30	65.78	-23.57	-2.87	-14.41	-11.37
BrF	NH_3	-65.08	99.36	-42.79	-6.74	-9.69	-24.95
ClF	NH_3	-66.71	117.57	-55.41	-9.29	-13.55	-27.38
I_2	NH_3	-34.41	54.26	-20.40	-3.91	-9.47	-13.93
Br_2	NH_3	-44.80	74.01	-26.27	-4.89	-11.14	-13.08
Cl_2	NH_3	-28.73	49.22	-16.04	-3.08	-11.31	-9.93
BrF	H_2S	-29.82	53.55	-23.05	-3.94	-10.75	-14.02
ClF	H_2S	-29.49	59.58	-25.43	-3.69	-13.52	-12.55
I_2	H_2S	-10.48	18.10	-6.71	-0.69	-5.72	-5.51
Br_2	H_2S	-11.09	19.36	-6.14	-0.69	-6.38	-4.94
Cl_2	H_2S	-7.39	13.30	-3.67	-0.39	-5.24	-3.40
BrF	Me_2O	-29.49	43.08	-16.42	-2.39	-8.35	-13.56
ClF	Me_2O	-23.88	38.25	-13.45	-1.84	-9.96	-10.88
I_2	Me_2O	-14.89	21.20	-6.55	-0.55	-8.98	-9.76
Br_2	Me_2O	-13.52	19.64	-5.19	-0.43	-6.10	-5.61
Cl_2	Me_2O	-9.52	14.27	-3.27	-0.26	-6.09	-4.87
BrF	H_2O	-20.31	29.97	-10.53	-2.23	-6.42	-9.10
ClF	H_2O	-11.69	16.58	-4.98	-1.41	-4.84	-5.81
I_2	H_2O	-9.34	12.96	-3.91	-0.71	-3.88	-4.65
Br_2	H_2O	-7.31	9.85	-2.47	-0.56	-3.36	-3.54
Cl_2	H_2O	-4.97	6.53	-1.45	-0.34	-2.42	-2.38
BrF	HCN	-21.86	30.03	-10.12	-1.80	-5.47	-9.65
ClF	HCN	-15.51	22.33	-6.71	-0.89	-6.34	-7.64
I_2	HCN	-11.74	15.42	-4.15	-0.46	-2.26	-3.45
Br_2	HCN	-9.83	13.01	-3.07	-0.25	-3.43	-3.87
Cl_2	HCN	-7.05	9.53	-2.03	-0.07	-3.09	-2.98

Table S7. The GKS-EDA results with ε=7.22 calculated at ωB97X-D/ACCD. (kcal/mol)

XB donor	XB acceptor	ΔG^{ele}	ΔG^{Pauli}	ΔG^{pol}	ΔG^{desol}	$\Delta G^{corr+disp}$	ΔG^{int}
BrF	pyridine	-79.87	127.52	-58.02	-9.19	-13.36	-32.92
ClF	pyridine	-95.53	176.23	-92.47	-12.49	-15.80	-40.06
I_2	pyridine	-39.90	65.99	-25.86	-3.43	-11.41	-14.61
Br_2	pyridine	-54.60	93.78	-35.33	-5.14	-14.61	-15.89
Cl_2	pyridine	-112.96	224.75	-118.23	-15.79	-15.54	-37.77
BrF	NH_3	-71.22	109.82	-47.06	-8.69	-10.16	-27.32
ClF	NH_3	-75.86	135.73	-65.16	-12.62	-13.97	-31.88
I_2	NH_3	-38.38	61.80	-22.90	-5.19	-10.31	-14.98
Br_2	NH_3	-46.25	76.54	-26.59	-5.95	-11.87	-14.13
Cl_2	NH_3	-108.56	215.67	-108.62	-19.78	-12.51	-33.81
BrF	H_2S	-33.28	60.67	-25.93	-5.26	-11.74	-15.55
ClF	H_2S	-30.29	61.38	-25.89	-4.51	-14.17	-13.48
I_2	H_2S	-11.38	20.07	-7.37	-0.90	-6.11	-5.69
Br_2	H_2S	-11.15	19.49	-6.10	-0.81	-6.50	-5.06
Cl_2	H_2S	-7.56	13.66	-3.72	-0.47	-5.40	-3.49
BrF	Me_2O	-31.29	46.17	-17.37	-2.99	-8.80	-14.29
ClF	Me_2O	-24.23	38.79	-13.37	-2.18	-10.25	-11.24
I_2	Me_2O	-15.55	22.39	-6.87	-0.68	-9.16	-9.87
Br_2	Me_2O	-13.92	20.33	-5.31	-0.53	-6.28	-5.71
Cl_2	Me_2O	-9.58	14.35	-3.21	-0.30	-6.17	-4.92
BrF	H_2O	-21.94	32.83	-11.28	-2.77	-6.85	-9.50
ClF	H_2O	-12.27	17.51	-5.07	-1.71	-5.09	-6.01
I_2	H_2O	-9.60	13.35	-3.95	-0.87	-3.97	-4.71
Br_2	H_2O	-7.53	10.17	-2.47	-0.67	-3.45	-3.58
Cl_2	H_2O	-5.08	6.66	-1.41	-0.40	-2.47	-2.39
BrF	HCN	-23.12	32.21	-10.58	-2.26	-5.89	-10.15
ClF	HCN	-16.10	23.36	-6.82	-1.08	-6.67	-7.94
I_2	HCN	-12.16	16.16	-4.26	-0.55	-2.43	-3.57
Br_2	HCN	-10.14	13.55	-3.12	-0.31	-3.59	-3.97
Cl_2	HCN	-7.19	9.77	-2.02	-0.09	-3.19	-3.04

Table S8. GKS-EDA results for XB dimers in solution (ε=2.27) based on M06-2X/ACCD. (kcal/mol)

XB donor	XB acceptor	ΔG^{ele}	ΔG^{Pauli}	ΔG^{pol}	ΔG^{desol}	$\Delta G^{corr+disp}$	ΔG^{int}
BrF	pyridine	-64.69	102.80	-47.41	-4.22	-11.29	-24.81
ClF	pyridine	-61.80	110.23	-54.14	-4.32	-13.53	-23.57
I_2	pyridine	-38.01	63.65	-26.05	-1.98	-10.77	-13.17
Br_2	pyridine	-46.45	79.46	-30.31	-2.64	-13.07	-13.00
Cl_2	pyridine	-28.08	49.45	-17.69	-1.42	-10.66	-8.41
BrF	NH_3	-56.87	86.51	-38.14	-4.09	-8.30	-20.89
ClF	NH_3	-49.54	84.22	-38.98	-4.63	-10.64	-19.58
I_2	NH_3	-34.06	54.40	-21.69	-2.78	-8.94	-13.08
Br_2	NH_3	-37.43	60.87	-22.03	-2.98	-9.72	-11.28
Cl_2	NH_3	-19.79	31.75	-10.85	-1.33	-7.17	-7.39
BrF	H_2S	-26.05	46.27	-20.12	-2.30	-9.38	-11.58
ClF	H_2S	-15.33	27.83	-11.36	-1.06	-7.77	-7.69
I_2	H_2S	-10.57	18.46	-7.00	-0.50	-6.01	-5.62
Br_2	H_2S	-10.51	18.20	-5.84	-0.47	-6.57	-5.20
Cl_2	H_2S	-6.77	11.92	-3.60	-0.23	-5.02	-3.70
BrF	Me_2O	-27.38	39.83	-16.01	-1.34	-7.06	-11.96
ClF	Me_2O	-17.85	26.63	-10.01	-0.70	-7.27	-9.20
I_2	Me_2O	-15.54	22.77	-7.32	-0.35	-9.15	-9.59
Br_2	Me_2O	-13.14	19.30	-5.50	-0.19	-6.56	-6.10
Cl_2	Me_2O	-8.97	13.40	-3.49	-0.07	-6.19	-5.32
BrF	H_2O	-17.21	21.82	-8.84	-1.08	-3.24	-8.55
ClF	H_2O	-11.89	15.38	-5.72	-0.62	-4.30	-7.16
I_2	H_2O	-11.07	14.46	-4.79	-0.42	-2.89	-4.73
Br_2	H_2O	-9.10	11.89	-3.54	-0.32	-3.46	-4.52
Cl_2	H_2O	-6.65	8.83	-2.52	-0.19	-3.13	-3.66
BrF	HCN	-14.41	19.12	-7.99	-0.83	-3.88	-7.99
ClF	HCN	-9.07	11.66	-4.33	-0.39	-3.47	-5.59
I_2	HCN	-8.62	12.02	-4.29	-0.29	-3.66	-4.83
Br_2	HCN	-6.75	9.10	-2.79	-0.14	-3.19	-3.77
Cl_2	HCN	-4.82	6.48	-1.83	-0.05	-2.59	-2.83

Table S9. GKS-EDA results for XB dimers in solution (ε=4.18) based on M06-2X/ACCD. (kcal/mol)

XB donor	XB acceptor	ΔG^{ele}	ΔG^{Pauli}	ΔG^{pol}	ΔG^{desol}	$\Delta G^{corr+disp}$	ΔG^{int}
BrF	pyridine	-72.00	115.43	-53.61	-6.63	-11.52	-28.34
ClF	pyridine	-73.68	133.67	-68.04	-7.37	-13.57	-28.99
I_2	pyridine	-42.85	72.95	-29.96	-3.26	-11.40	-14.52
Br_2	pyridine	-57.04	99.36	-39.43	-4.80	-14.41	-16.31
Cl_2	pyridine	-50.83	96.05	-40.31	-4.53	-14.92	-14.54
BrF	NH_3	-64.89	100.17	-44.13	-6.51	-8.56	-23.93
ClF	NH_3	-66.58	118.22	-57.97	-8.92	-10.85	-26.10
I_2	NH_3	-40.12	65.94	-26.26	-4.68	-9.60	-14.71
Br_2	NH_3	-55.20	94.28	-36.24	-6.47	-11.60	-15.23
Cl_2	NH_3	-33.99	60.04	-21.93	-3.79	-10.72	-10.39
BrF	H_2S	-30.33	55.04	-24.04	-3.84	-10.31	-13.49
ClF	H_2S	-24.82	49.16	-20.98	-2.77	-10.73	-10.14
I_2	H_2S	-11.46	20.49	-7.71	-0.81	-6.48	-5.96
Br_2	H_2S	-12.70	22.74	-7.25	-0.86	-7.57	-5.63
Cl_2	H_2S	-6.95	12.37	-3.69	-0.33	-5.20	-3.81
BrF	Me_2O	-30.23	44.73	-17.73	-2.13	-7.49	-12.85
ClF	Me_2O	-20.85	32.21	-12.02	-1.22	-7.94	-9.82
I_2	Me_2O	-16.50	24.47	-7.85	-0.55	-9.38	-9.81
Br_2	Me_2O	-13.84	20.49	-5.79	-0.30	-6.74	-6.18
Cl_2	Me_2O	-9.31	13.97	-3.62	-0.12	-6.32	-5.41
BrF	H_2O	-18.91	24.63	-9.67	-1.66	-3.41	-9.02
ClF	H_2O	-12.64	16.60	-6.00	-0.92	-4.48	-7.45
I_2	H_2O	-11.75	15.63	-5.07	-0.64	-3.02	-4.85
Br_2	H_2O	-9.53	12.62	-3.66	-0.46	-3.59	-4.63
Cl_2	H_2O	-6.84	9.13	-2.54	-0.27	-3.20	-3.73
BrF	HCN	-15.95	21.56	-8.63	-1.26	-4.10	-8.37
ClF	HCN	-9.68	12.48	-4.40	-0.57	-3.61	-5.78
I_2	HCN	-9.06	12.73	-4.41	-0.42	-3.78	-4.94
Br_2	HCN	-7.06	9.51	-2.78	-0.21	-3.30	-3.83
Cl_2	HCN	-5.01	6.68	-1.79	-0.08	-2.67	-2.85

Table S10. GKS-EDA results for XB dimers in solution (ε=7.22) based on M06-2X/ACCD. (kcal/mol)

XB donor	XB acceptor	ΔG^{ele}	ΔG^{Pauli}	ΔG^{pol}	ΔG^{desol}	$\Delta G^{corr+disp}$	ΔG^{int}
BrF	pyridine	-76.96	123.98	-57.97	-8.38	-11.54	-30.87
ClF	pyridine	-83.11	152.36	-79.83	-9.97	-13.05	-33.60
I_2	pyridine	-46.55	80.14	-33.13	-4.28	-11.76	-15.57
Br_2	pyridine	-64.83	114.04	-46.63	-6.61	-14.94	-18.96
Cl_2	pyridine	-79.22	154.86	-75.46	-9.42	-14.71	-23.96
BrF	NH_3	-70.37	109.54	-48.43	-8.29	-8.59	-26.14
ClF	NH_3	-68.10	120.86	-59.36	-10.69	-10.75	-28.04
I_2	NH_3	-44.43	74.26	-29.70	-6.17	-9.91	-15.95
Br_2	NH_3	-56.71	96.93	-37.26	-7.85	-11.75	-16.64
Cl_2	NH_3	-51.31	95.56	-39.43	-7.46	-12.62	-15.26
BrF	H_2S	-33.20	60.98	-26.87	-5.03	-10.80	-14.93
ClF	H_2S	-25.59	50.90	-21.74	-3.39	-11.01	-10.83
I_2	H_2S	-12.40	22.57	-8.42	-1.05	-6.88	-6.17
Br_2	H_2S	-12.92	23.23	-7.32	-1.02	-7.76	-5.80
Cl_2	H_2S	-7.12	12.74	-3.78	-0.40	-5.34	-3.89
BrF	Me_2O	-32.15	48.07	-18.92	-2.70	-7.78	-13.48
ClF	Me_2O	-21.13	32.63	-12.05	-1.45	-8.04	-10.05
I_2	Me_2O	-17.15	25.65	-8.22	-0.69	-9.54	-9.95
Br_2	Me_2O	-14.80	22.19	-6.27	-0.41	-6.96	-6.25
Cl_2	Me_2O	-9.36	14.02	-3.59	-0.14	-6.36	-5.43
BrF	H_2O	-20.21	26.85	-10.34	-2.09	-3.54	-9.34
ClF	H_2O	-13.13	17.42	-6.20	-1.12	-4.60	-7.64
I_2	H_2O	-12.21	16.44	-5.27	-0.78	-3.10	-4.92
Br_2	H_2O	-9.80	13.07	-3.74	-0.56	-3.67	-4.69
Cl_2	H_2O	-6.97	9.36	-2.57	-0.32	-3.26	-3.77
BrF	HCN	-17.04	23.34	-9.12	-1.57	-4.25	-8.63
ClF	HCN	-10.07	13.02	-4.46	-0.70	-3.70	-5.90
I_2	HCN	-9.34	13.18	-4.49	-0.51	-3.85	-5.00
Br_2	HCN	-7.24	9.76	-2.78	-0.25	-3.36	-3.87
Cl_2	HCN	-5.11	6.80	-1.76	-0.09	-2.71	-2.86

Table S11. GKS-EDA results for XB dimers in solution (ε=78.36) based on M06-2X/ACCD. (kcal/mol)

XB donor	XB acceptor	ΔG^{ele}	ΔG^{Pauli}	ΔG^{pol}	ΔG^{desol}	$\Delta G^{corr+disp}$	ΔG^{int}
BrF	pyridine	-83.44	135.10	-63.89	-10.88	-11.39	-34.50
ClF	pyridine	-97.72	181.30	-99.27	-14.48	-11.37	-41.54
I_2	pyridine	-51.77	90.33	-37.81	-5.86	-12.10	-17.21
Br_2	pyridine	-80.08	142.84	-61.79	-10.18	-15.02	-24.22
Cl_2	pyridine	-142.90	286.11	-170.96	-25.77	-1.63	-55.15
BrF	NH_3	-78.26	123.11	-54.92	-10.94	-8.40	-29.42
ClF	NH_3	-81.83	148.33	-76.37	-15.64	-9.46	-34.97
I_2	NH_3	-51.08	87.22	-35.35	-8.60	-10.14	-17.96
Br_2	NH_3	-71.02	124.03	-50.44	-12.08	-11.76	-21.28
Cl_2	NH_3	-88.87	174.05	-86.75	-17.34	-9.44	-28.34
BrF	H_2S	-37.61	70.14	-31.51	-6.92	-11.32	-17.24
ClF	H_2S	-33.03	67.97	-30.80	-5.59	-12.48	-13.94
I_2	H_2S	-14.17	26.53	-9.79	-1.49	-7.60	-6.53
Br_2	H_2S	-15.31	28.24	-8.84	-1.53	-8.87	-6.31
Cl_2	H_2S	-7.39	13.34	-3.92	-0.49	-5.52	-3.98
BrF	Me_2O	-34.76	52.63	-20.59	-3.52	-8.15	-14.38
ClF	Me_2O	-23.55	37.21	-13.70	-2.01	-8.61	-10.67
I_2	Me_2O	-18.02	27.25	-8.71	-0.88	-9.76	-10.14
Br_2	Me_2O	-14.84	22.22	-6.20	-0.48	-7.02	-6.32
Cl_2	Me_2O	-9.56	14.35	-3.65	-0.18	-6.45	-5.49
BrF	H_2O	-22.12	30.17	-11.37	-2.73	-3.76	-9.80
ClF	H_2O	-13.86	18.67	-6.52	-1.40	-4.77	-7.88
I_2	H_2O	-12.79	17.49	-5.53	-0.98	-3.21	-5.02
Br_2	H_2O	-10.13	13.65	-3.85	-0.68	-3.77	-4.78
Cl_2	H_2O	-7.11	9.59	-2.59	-0.38	-3.33	-3.82
BrF	HCN	-18.80	26.38	-10.01	-2.03	-4.51	-8.98
ClF	HCN	-10.56	13.71	-4.52	-0.86	-3.82	-6.05
I_2	HCN	-9.69	13.76	-4.60	-0.61	-3.94	-5.08
Br_2	HCN	-7.45	10.05	-2.78	-0.31	-3.43	-3.92
Cl_2	HCN	-5.24	6.95	-1.72	-0.11	-2.75	-2.87

Table S12. The weights of the attractive interactions in benzene, ethylphenyl ether and dibromomethane.

	XB donor	XB acceptor	ε=2.27					ε=4.18					ε=7.22				
			W^{pol}	W^{ele}	W^{desol}	$W^{disp/corr}$	$\Delta G^{int}/\Delta E^{int}$	W^{pol}	W^{ele}	W^{desol}	$W^{disp/corr}$	$\Delta G^{int}/\Delta E^{int}$	W^{pol}	W^{ele}	W^{desol}	$W^{disp/corr}$	$\Delta G^{int}/\Delta E^{int}$
Type A	ClF	pyridine	41%	46%	3%	10%	158%	42%	45%	5%	9%	198%	43%	44%	6%	7%	233%
	ClF	NH_3	37%	47%	5%	11%	153%	38%	46%	6%	9%	195%	39%	45%	8%	8%	227%
	ClF	H_2S	32%	42%	3%	22%	135%	35%	41%	5%	19%	182%	35%	40%	6%	19%	196%
	BrF	pyridine	36%	51%	3%	9%	133%	36%	50%	5%	9%	153%	36%	50%	6%	8%	168%
	BrF	NH_3	35%	53%	4%	8%	133%	34%	52%	5%	8%	151%	34%	52%	6%	7%	166%
	BrF	H_2S	34%	45%	4%	17%	133%	34%	44%	6%	16%	154%	34%	44%	7%	15%	170%
	Cl_2	NH_3	26%	50%	4%	21%	131%	27%	49%	5%	19%	159%	29%	47%	6%	17%	196%
	Cl_2	pyridine	28%	48%	2%	21%	131%	31%	47%	4%	19%	169%	45%	43%	6%	6%	560%
	Br_2	NH_3	28%	53%	4%	15%	131%	30%	51%	6%	13%	164%	29%	51%	7%	13%	177%
	Br_2	pyridine	30%	51%	3%	16%	129%	31%	54%	4%	14%	154%	32%	50%	5%	13%	179%
	I_2	NH_3	30%	51%	4%	15%	122%	30%	50%	6%	14%	136%	30%	50%	7%	13%	146%
	BrF	H_2O	26%	56%	4%	14%	121%	26%	55%	6%	14%	131%	25%	55%	7%	14%	138%
	ClF	H_2O	23%	52%	3%	21%	117%	22%	52%	5%	21%	125%	22%	51%	5%	21%	130%
	BrF	Me_2O	29%	53%	3%	15%	119%	29%	52%	4%	15%	129%	29%	52%	5%	15%	136%
	ClF	Me_2O	27%	49%	3%	21%	118%	27%	49%	4%	20%	131%	27%	48%	4%	20%	135%
	I_2	pyridine	32%	50%	2%	15%	117%	32%	50%	4%	15%	126%	32%	50%	4%	14%	134%
	BrF	HCN	28%	52%	3%	17%	117%	27%	52%	5%	16%	125%	27%	52%	5%	16%	130%
	ClF	HCN	23%	52%	3%	21%	113%	22%	52%	4%	22%	119%	22%	52%	5%	22%	123%
Type B	I_2	H_2S	28%	45%	2%	25%	111%	28%	44%	3%	24%	117%	29%	44%	3%	24%	121%
	Br_2	H_2S	25%	46%	2%	27%	113%	25%	46%	3%	26%	119%	25%	45%	3%	26%	122%
	Cl_2	H_2S	22%	45%	2%	31%	112%	22%	44%	2%	31%	117%	22%	44%	3%	31%	120%
	I_2	H_2O	23%	63%	3%	11%	113%	22%	62%	4%	12%	119%	22%	62%	4%	12%	123%
	Br_2	H_2O	19%	59%	2%	20%	111%	18%	58%	3%	20%	115%	18%	58%	4%	20%	118%
	Cl_2	H_2O	17%	57%	2%	24%	109%	16%	56%	3%	25%	112%	16%	56%	3%	25%	114%
	I_2	Me_2O	21%	48%	1%	30%	105%	21%	48%	2%	29%	107%	21%	48%	2%	28%	108%
	Br_2	Me_2O	21%	54%	1%	24%	106%	21%	54%	2%	24%	109%	20%	53%	2%	24%	111%
	Cl_2	Me_2O	17%	50%	1%	32%	106%	17%	50%	1%	32%	109%	17%	50%	2%	32%	110%

	I_2	HCN	23%	53%	2%	22%	106%	22%	53%	3%	22%	109%	22%	53%	3%	22%	110%
	Br_2	HCN	19%	54%	1%	25%	105%	18%	55%	2%	25%	107%	18%	55%	2%	25%	108%
	Cl_2	HCN	18%	55%	1%	27%	102%	16%	56%	1%	27%	103%	16%	56%	1%	27%	103%