Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Hydrogen and Halogen Bonds are Ruled by the Same Mechanisms

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Electronic supplementary information

All results presented were obtained at MP2/6-311++G(d,p) level, QTAIM was applied to calculate charges as well as to localize bond critical points and to analyze their characteristics.
s%, Pol, and E_{NBO} were obtained with the use of NBO method.
T1 diagnostic for all systems considered here suggests that the other configurations are not important (T1 < 0.01 for all systems)

Table. Results for $HOH\ldots OH_2$ water dimer

H…O	s%	Pol	E_{NBO}	Q(H)	V(H)	ρ_{BCP}	V_{BCP}	G_{BCP}	$\nabla^2\rho_{BCP}$
2.6	23.6	73.8	0.5	0.589	3.3	0.006	-0.003	0.004	0.019
2.5	23.7	73.9	0.8	0.591	3.2	0.007	-0.004	0.005	0.024
2.4	24.0	74.0	1.2	0.594	3.0	0.009	-0.005	0.006	0.030
2.3	24.2	74.1	1.8	0.597	2.9	0.011	-0.007	0.008	0.038
2.2	24.5	74.2	2.6	0.600	2.7	0.013	-0.009	0.011	0.049
2.1	24.9	74.4	3.9	0.604	2.6	0.017	-0.012	0.014	0.063
2	25.4	74.6	5.7	0.608	2.4	0.021	-0.016	0.018	0.081
1.95*	25.7	74.7	6.9	0.611	2.3	0.023	-0.018	0.021	0.091
1.9	25.9	74.8	8.4	0.613	2.2	0.026	-0.021	0.024	0.102
1.8	26.6	75.0	12.2	0.618	2.0	0.033	-0.030	0.031	0.128
1.7	27.3	75.3	17.7	0.624	1.8	0.042	-0.043	0.041	0.156
**	23.0	72.9	-	0.567	3.5	-	-	-	

Designations:
* - for the energetic minimum of the complex
** - the parameters for the H_2O monomer not participating in intermolecular interactions
H…O – H…O distance (in Å)
s% - percentage contribution of s-character in O-atom orbital of the O-H proton donating bond
Pol- polarization of the O-H proton donating bond (% at O-atom)
E_{NBO} – energy corresponding to the $n_O \rightarrow \sigma^*_{OH}$ (in kcal/mol)
Q(H) – QTAIM charge of the H-atom of the proton donating OH bond (au)
V(H) - QTAIM volume of the H-atom of the proton donating OH bond (in $Å^3$)
ρ_{BCP}, V_{BCP}, G_{BCP} and $\nabla^2\rho_{BCP}$ – QTAIM parameters (in au) corresponding to the intermolecular H…O bond critical point: the electron density at BCP, the potential electron energy density at BCP, the kinetic electron energy density at BCP and the laplacian of the electron density at BCP, respectively.

Table. Results for NH_4^+…NH_3 complex

H…N	s%	Pol	E_{NBO}	Q(H)	V(H)	ρ_{BCP}	V_{BCP}	G_{BCP}	$\nabla^2\rho_{BCP}$
2.7	26.2	74.4	2.3	0.533	3.7	0.007	-0.003	0.004	0.017
2.4	27.0	75.0	5.9	0.541	3.3	0.013	-0.006	0.007	0.031
2.1	28.3	75.8	14.6	0.550	2.9	0.023	-0.013	0.014	0.056
2	28.7	76.1	19.6	0.553	2.7	0.029	-0.019	0.017	0.065
1.9	29.1	76.5	26.1	0.557	2.5	0.036	-0.026	0.022	0.074
1.8	29.4	76.9	34.9	0.560	2.4	0.045	-0.037	0.028	0.080
1.7	29.6	77.3	46.7	0.564	2.2	0.057	-0.052	0.036	0.080
1.6	29.6	78.0	63.1	0.568	2.1	0.072	-0.071	0.045	0.070
1.58*	29.6	78.2	67.7	0.569	2.1	0.076	-0.077	0.047	0.066
1.5	29.3	78.9	86.9	0.571	2.0	0.092	-0.097	0.054	0.041
**	25.0	72.9	-	0.508	3.7	-	-	-	-

Designations:

* - for the energetic minimum of the complex

** - the parameters for the NH_4^+ monomer not participating in intermolecular interactions

H…N – H…N distance (in Å)

s% - percentage contribution of s-character in N-atom orbital of the N-H proton donating bond

Pol- polarization of the N-H proton donating bond (% at N-atom)

E_{NBO} – energy corresponding to the $n_N \rightarrow \sigma^*_{NH}$ (in kcal/mol)

Q(H) – QTAIM charge of the H-atom of the proton donating NH bond (au)

V(H) - QTAIM volume of the H-atom of the proton donating NH bond (in $Å^3$)

ρ_{BCP}, V_{BCP}, G_{BCP} and $\nabla^2\rho_{BCP}$ – QTAIM parameters (in au) corresponding to the intermolecular H…N bond critical point: the electron density at BCP, the potential electron energy density at BCP, the kinetic electron energy density at BCP and the laplacian of the electron density at BCP, respectively.

Table. Results for $F_3CCl\ldots NH_3$ complex

Cl…N	s%	Pol	E_{NBO}	Q(Cl)	V(Cl)	ρ_{BCP}	V_{BCP}	G_{BCP}	$\nabla^2\rho_{BCP}$
3.4	27.4	47.9	0.8	-0.056	30.5	0.006	-0.004	0.005	0.006
3.3	27.4	47.9	1.1	-0.054	30.4	0.007	-0.005	0.006	0.007
3.2	27.5	48.0	1.5	-0.052	30.2	0.009	-0.006	0.007	0.008
3.1	27.6	48.1	2.1	-0.050	30.0	0.011	-0.007	0.008	0.010
3.09*	27.6	48.1	2.2	-0.050	30.0	0.011	-0.007	0.009	0.010
3.05	27.6	48.1	2.4	-0.049	30.0	0.012	-0.008	0.009	0.010
3	27.7	48.1	2.8	-0.048	29.9	0.013	-0.009	0.010	0.012
2.9	27.8	48.2	3.6	-0.045	29.8	0.016	-0.011	0.013	0.014
2.8	28.0	48.4	4.7	-0.042	29.6	0.019	-0.014	0.016	0.017
2.7	28.1	48.5	6.2	-0.038	29.3	0.023	-0.018	0.019	0.021
**	26.6	47.0	-	-0.086	30.7	-	-	-	-

Designations:

* - for the energetic minimum of the complex

** - the parameters for the F_3CCl monomer not participating in intermolecular interactions

Cl…N – Cl…N distance (in Å)

s% - percentage contribution of s-character in C-atom orbital of the C-Cl bond of the Lewis acid unit

Pol- polarization of the C-Cl bond (% at C-atom)

E_{NBO} – energy corresponding to the $n_N \rightarrow \sigma^*_{CCl}$ (in kcal/mol)

Q(Cl) – QTAIM charge of the Cl-atom of the CCl bond (au)

V(Cl) - QTAIM volume of the Cl-atom of the CCl bond (in $Å^3$)

ρ_{BCP}, V_{BCP}, G_{BCP} and $\nabla^2\rho_{BCP}$ – QTAIM parameters (in au) corresponding to the intermolecular Cl…N bond critical point: the electron density at BCP, the potential electron energy density at BCP, the kinetic electron energy density at BCP and the laplacian of the electron density at BCP, respectively.

Table. Results for $F_3CCl\ldots OH^-$ complex

Cl…O	s%	Pol	E_{NBO}	Q(Cl)	V(Cl)	ρ_{BCP}	V_{BCP}	G_{BCP}	$\nabla^2\rho_{BCP}$
3	30.3	50.7	4.5	0.049	29.7	0.012	-0.008	0.009	0.039
2.9	30.5	50.8	5.5	0.054	29.4	0.014	-0.010	0.011	0.047
2.8	30.7	51.0	6.7	0.059	29.3	0.017	-0.012	0.013	0.057
2.7	30.9	51.2	8.5	0.063	29.2	0.021	-0.015	0.016	0.070
2.6	31.2	51.5	10.8	0.068	29.0	0.025	-0.019	0.020	0.088
2.5	31.4	51.8	14.0	0.071	28.7	0.031	-0.024	0.025	0.109
2.46*	31.6	51.9	15.7	0.072	28.7	0.034	-0.026	0.028	0.118
2.4	31.7	52.1	18.7	0.073	28.6	0.038	-0.030	0.032	0.134
2.3	32.0	52.6	25.4	0.073	28.5	0.048	-0.040	0.040	0.163
2.2	32.3	53.4	34.5	0.071	28.5	0.060	-0.053	0.051	0.195
**	26.6	47.0	-	-0.086	30.7	-	-	-	

Designations:

* - for the energetic minimum of the complex

** - the parameters for the F_3CCl monomer not participating in intermolecular interactions

Cl…O – Cl…O distance (in Å)

s% - percentage contribution of s-character in C-atom orbital of the C-Cl bond of the Lewis acid unit

Pol- polarization of the C-Cl bond (% at C-atom)

E_{NBO} – energy corresponding to the $n_O \rightarrow \sigma^*_{CCl}$ (in kcal/mol)

Q(Cl) – QTAIM charge of the Cl-atom of the CCl bond (au)

V(Cl) - QTAIM volume of the Cl-atom of the CCl bond (in $Å^3$)

ρ_{BCP}, V_{BCP}, G_{BCP} and $\nabla^2\rho_{BCP}$ – QTAIM parameters (in au) corresponding to the intermolecular Cl…O bond critical point: the electron density at BCP, the potential electron energy density at BCP, the kinetic electron energy density at BCP and the laplacian of the electron density at BCP, respectively.

Table. Results for HOH…OH_2 water dimer, DFT/NEDA terms of the interaction energy (in kcal/mol), CT/ES and PL/ES are the ratios of the energy contributions (see eq.4 in the main text).

H…O	TOT	CT	ES	PL	XC	DEF	CT/ES	PL/ES
1.7	-3.67	-20.09	-13.89	-5.07	-5.02	40.4	1.45	0.37
1.8	-4.52	-14.21	-11.4	-4.79	-4.05	29.93	1.25	0.42
1.9	-4.88	-10.1	-9.49	-4.33	-3.23	22.27	1.06	0.46
1.95	-4.95	-8.52	-8.68	-4.06	-2.87	19.18	0.98	0.47
2	-4.96	-7.19	-7.96	-3.79	-2.54	16.52	0.90	0.48
2.1	-4.84	-5.2	-6.8	-3.14	-1.97	12.27	0.76	0.46
2.2	-4.61	-3.76	-5.84	-2.63	-1.5	9.12	0.64	0.45
2.3	-4.32	-2.77	-5.07	-2.15	-1.14	6.81	0.55	0.42
2.4	-3.99	-2.08	-4.44	-1.75	-0.84	5.12	0.47	0.39
2.5	-3.67	-1.58	-3.92	-1.43	-0.62	3.88	0.40	0.36
2.6	-3.35	-1.23	-3.48	-1.18	-0.45	2.99	0.35	0.34

Table. Results for NH_4^+…NH_3 complex, DFT/NEDA terms of the interaction energy (in kcal/mol), CT/ES and PL/ES are the ratios of the energy contributions (see eq.4 in the main text).

H…N	TOT	CT	ES	PL	XC	DEF	CT/ES	PL/ES
1.5	-33.06	-85.6	-41.94	-1.8	-7.64	103.92	2.04	0.04
1.58	-30.87	-68.86	-37.96	-2.83	-6.57	85.35	1.81	0.07
1.6	-30.34	-64.66	-36.88	-3.11	-6.3	80.61	1.75	0.08
1.7	-28.59	-49.31	-32.55	-4.18	-5.23	62.68	1.51	0.13
1.8	-27.19	-37.82	-28.9	-4.94	-4.3	48.77	1.31	0.17
1.9	-25.86	-29.08	-25.85	-5.35	-3.54	37.96	1.12	0.21
2	-24.52	-22.37	-23.28	-5.44	-2.85	29.42	0.96	0.23
2.1	-23.18	-17.23	-21.11	-5.29	-2.25	22.7	0.82	0.25
2.4	-19.2	-8.07	-16.32	-4.14	-0.96	10.29	0.49	0.25
2.7	-15.7	-4.16	-13.14	-2.97	-0.32	4.89	0.32	0.23

Table. Results for $F_3CCl\cdots NH_3$ complex, DFT/NEDA terms of the interaction energy (in kcal/mol), CT/ES and PL/ES are the ratios of the energy contributions (see eq.4 in the main text).

Cl…N	TOT	CT	ES	PL	XC	DEF	CT/ES	PL/ES
2.7	-0.7	-10.88	-11.35	-30.6	-9.03	61.16	0.96	2.70
2.8	-1.35	-8.39	-8.93	-24.4	-7.17	47.54	0.94	2.73
2.9	-1.74	-6.53	-7.12	-19.17	-5.64	36.72	0.92	2.69
3	-1.92	-5.13	-5.72	-14.9	-4.41	28.24	0.90	2.60
3.05	-1.95	-4.55	-5.15	-13.09	-3.89	24.73	0.88	2.54
3.09	-1.96	-4.19	-4.78	-11.94	-3.55	22.5	0.88	2.50
3.1	-1.96	-4.05	-4.65	-11.48	-3.42	21.64	0.87	2.47
3.2	-1.92	-3.21	-3.81	-8.74	-2.62	16.46	0.84	2.29
3.3	-1.84	-2.56	-3.17	-6.66	-2	12.55	0.81	2.10
3.4	-1.73	-2.06	-2.66	-5.05	-1.51	9.55	0.77	1.90

Table. Results for $F_3CCl\cdots OH^-$ complex, DFT/NEDA terms of the interaction energy (in kcal/mol), CT/ES and PL/ES are the ratios of the energy contributions (see eq.4 in the main text).

Cl…O	TOT	CT	ES	PL	XC	DEF	CT/ES	PL/ES
2.2	-20.39	-56.06	-56.45	-89.01	-25.67	206.8	0.99	1.58
2.3	-20.39	-42.46	-45.21	-76.47	-21.23	164.98	0.94	1.69
2.4	-19.98	-32.41	-36.53	-65.48	-17.5	131.94	0.89	1.79
2.46	-19.59	-27.76	-32.41	-59.53	-15.56	115.67	0.86	1.84
2.5	-19.27	-25	-29.93	-55.65	-14.32	105.63	0.84	1.86
2.6	-18.37	-19.6	-25.06	-46.85	-11.69	84.83	0.78	1.87
2.7	-17.37	-15.61	-21.46	-38.93	-9.46	68.09	0.73	1.81
2.8	-16.29	-12.53	-18.52	-32.25	-7.63	54.64	0.68	1.74
2.9	-15.22	-10.22	-16.27	-26.5	-6.13	43.9	0.63	1.63

Table. The linear correlation coefficients for the relations between the binding energy (E_{bin}, in kcal/mol) or the electron density at H(X)…B BCP, ρ_{BCP} (in au) and the energy terms (kcal/mol) obtained within DFT/NEDA scheme.

Ebin vs →	TOT	CT	ES	PL	XC	DEF
H-bonds	1.00	0.98	0.99	0.69	0.97	1.00
X-bonds	1.00	0.97	0.98	0.99	1.00	0.99
ρBCP vs →	TOT	CT	ES	PL	XC	DEF
H-bonds	0.98	0.99	0.96	0.57	0.92	0.97
X-bonds	1.00	0.99	1.00	0.98	1.00	1.00