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

Electronic Supplementary Information for "On the directionality and non-linearity of hydrogen and halogen bonds"

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1 Convergence of interaction energies

Table SI Convergence of the CP-CCSD(T)-F12b/aug-cc-pV(*n*+d)Z (n = D, T, Q) interaction energies (kcal mol^{-1}) for a systematic series of hydrogen and halogen bonded complexes. Values in parentheses indicate the basis set superposition error.

Acceptor	Lewis base	DZ	TZ	QZ[a]
HCl	Formaldehyde	–5.35 (0.42)	–5.56 (0.22)	–5.67 (0.10)
	Vinyl fluoride	–2.88 (0.37)	–3.03 (0.19)	–3.09 (0.08)
	Oxirane	–6.98 (0.58)	–7.23 (0.32)	–7.37 (0.13)
	Thiirane	–5.97 (0.69)	–6.27 (0.36)	–6.41 (0.12)
	Methylenecyclopropane	–3.99 (0.60)	–4.22 (0.30)	–4.29 (0.11)
	2,5-dihydrofuran	–7.72 (0.69)	–8.02 (0.39)	–8.16 (0.16)
HCCH	Formaldehyde	–3.05 (0.31)	–3.15 (0.12)	–3.19 (0.05)
	Vinyl fluoride	–1.91 (0.32)	–2.01 (0.12)	–2.04 (0.05)
	Oxirane	–3.73 (0.42)	–3.85 (0.17)	–3.90 (0.07)
	Thiirane	–3.32 (0.56)	–3.49 (0.21)	–3.54 (0.07)
	Methylenecyclopropane	–2.50 (0.50)	–2.62 (0.17)	–2.65 (0.06)
	2,5-dihydrofuran	–3.76 (0.50)	–3.89 (0.22)	–3.93 (0.08)
ClF	Formaldehyde	–5.52 (0.41)	–5.80 (0.20)	–5.95 (0.09)
	Vinyl fluoride	–2.67 (0.33)	–2.83 (0.17)	–2.90 (0.08)
	Oxirane	–7.20 (0.57)	–7.55 (0.30)	–7.74 (0.14)
	Thiirane	–12.00 (0.92)	–12.63 (0.43)	–13.02 (0.17)
	Methylenecyclopropane	–6.01 (0.79)	–6.43 (0.37)	–6.61 (0.16)
	2,5-dihydrofuran	–8.01 (0.69)	–8.43 (0.37)	–8.63 (0.17)

[a] QZ calculations were performed ‘single-point’ on TZ optimised geometries, for all other basis sets the interaction energy was evaluated at the same level as the geometry optimisation.

2 SAPT decomposition at optimised geometries

Table SII SAPT decomposition of the interaction energies (kcal mol^{-1}) for the hydrogen and halogen bonding complexes.

Acceptor	Lewis base	E_{elec}	E_{exch}	E_{ind}	E_{disp}	Total
HCl	Formaldehyde	–9.51	12.76	–4.76	–4.07	–5.58
	Vinyl fluoride	–4.03	5.02	–1.39	–2.64	–3.04
	Oxirane	–13.07	18.81	–7.33	–5.75	–7.33
	Thiirane	–9.66	15.57	–6.38	–5.79	–6.27
	Methylenecyclopropane	–5.52	8.92	–3.34	–4.33	–4.28
	2,5-dihydrofuran	–14.93	22.07	–8.91	–6.44	–8.22
HCCH	Formaldehyde	–4.33	4.84	–1.05	–2.57	–3.11
	Vinyl fluoride	–2.37	2.77	–0.41	–1.99	–2.01
	Oxirane	–5.38	6.54	–1.46	–3.51	–3.81
	Thiirane	–4.41	6.07	–1.37	–3.80	–3.51
	Methylenecyclopropane	–2.85	4.29	–0.86	–3.24	–2.65
	2,5-dihydrofuran	–5.55	6.88	–1.69	–3.53	–3.89
ClF	Formaldehyde	–11.61	17.95	–6.51	–5.33	–5.50
	Vinyl fluoride	–3.64	5.23	–1.37	–3.01	–2.80
	Oxirane	–15.74	25.14	–9.36	–7.25	–7.21
	Thiirane	–36.67	67.61	–31.31	–12.29	–12.65
	Methylenecyclopropane	–14.83	28.08	–11.82	–8.14	–6.71
	2,5-dihydrofuran	–17.88	28.80	–10.72	–8.33	–8.12

3 NBO derived charge transfer

Table SIII Fraction of an electronic charge transferred from the Lewis base to the acceptor on complex formation. Total charges calculated using the NBO method based on the MP2/aug-cc-pV(T+d)Z density matrix.

Acceptor	Lewis base	Charge transfer
HCl	Formaldehyde	0.036
	Vinyl fluoride	0.009
	Oxirane	0.047
	Thiirane	0.068
	Methylenecyclopropane	0.018
	2,5-dihydrofuran	0.051
HCCH	Formaldehyde	0.011
	Vinyl fluoride	0.005
	Oxirane	0.014
	Thiirane	0.017
	Methylenecyclopropane	0.005
	2,5-dihydrofuran	0.015
ClF	Formaldehyde	0.046
	Vinyl fluoride	0.007
	Oxirane	0.058
	Thiirane	0.279
	Methylenecyclopropane	0.075
	2,5-dihydrofuran	0.061

4 Definition of angular geometries

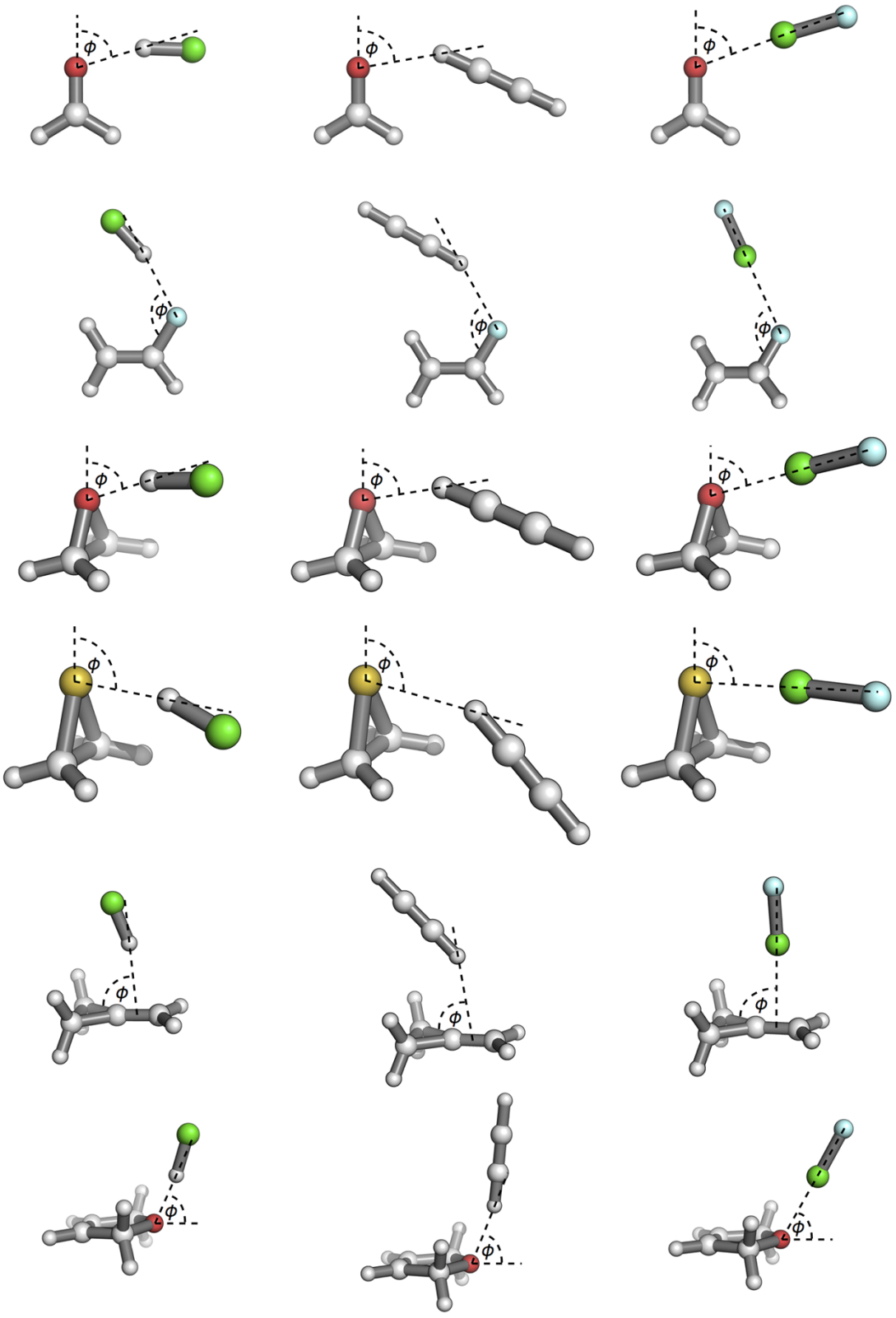

Figure S1 Definition of the angular geometry φ for the B···HCl (left column), B···HCCH (centre column) and B···ClF (right column) complexes.

5 Cartesian coordinates of optimised structures

5.1 B···HCl

Formaldehyde···HCl
6
CCSD(T)-F12B/AVTZ+D ENERGY=-574.74738669

O	-1.4800347767	-0.6595382255	0.0000000000
C	-1.9431076547	0.4598142407	0.0000000000
H	-1.2926512628	1.3474748341	0.0000000000
H	-3.0294832558	0.6244877579	0.0000000000
H	0.3940393570	-0.4544544967	0.0000000000
Cl	1.5730645931	0.0780878895	0.0000000000

Vinyl fluoride···HCl
8
CCSD(T)-F12B/AVTZ+D ENERGY=-638.00219347

F	1.4487615739	0.2563237106	0.0000000000
C	1.1871285396	1.5850644555	0.0000000000
C	-0.0539079893	2.0451439010	0.0000000000
H	2.0951652585	2.1697343803	0.0000000000
H	-0.9066121080	1.3813056906	0.0000000000
H	-0.2082941938	3.1133448607	0.0000000000
H	-0.0839140524	-1.1295808961	0.0000000000
Cl	-1.2269910289	-1.7065401025	0.0000000000

Oxirane···HCl
9
CCSD(T)-F12B/AVTZ+D ENERGY=-613.97408789

O	0.9977426480	0.0000000000	-0.7781675103
C	1.5579625206	-0.7314170737	0.3286154689
C	1.5579625206	0.7314170737	0.3286154689
H	2.4668283799	1.2674240244	0.0884179582
H	0.8259971970	1.2563381812	0.9310545530
H	0.8259971970	-1.2563381812	0.9310545530
H	2.4668283799	-1.2674240244	0.0884179582
H	-0.7550032963	0.0000000000	-0.5094601895
Cl	-1.9474555466	0.0000000000	0.0168857400

Thiirane···HCl
9
CCSD(T)-F12B/AVTZ+D ENERGY=-936.60578351

S	-1.2062862599	0.8026999473	0.0000000000
C	-1.2080310969	-0.8607450475	0.7406689795
C	-1.2080310969	-0.8607450475	-0.7406689795
H	-2.1243664165	-1.1198565624	-1.2527629857
H	-0.2877751560	-1.1287262874	-1.2435049960
H	-0.2877751560	-1.1287262874	1.2435049960
H	-2.1243664165	-1.1198565624	1.2527629857
H	1.0442218567	0.6180923762	0.0000000000
Cl	2.2258767420	0.0710184713	0.0000000000

Methylenecyclopropane···HCl
12
CCSD(T)-F12B/AVTZ+D ENERGY=-616.08684362

C	1.8470328019	0.6520751447	0.0000000000
C	0.6126151536	1.1389449407	0.0000000000
C	-0.5571927696	1.5757336743	0.7700620128
C	-0.5571927696	1.5757336743	-0.7700620128
H	2.3686384183	0.4549570237	0.9288145723
H	2.3686384183	0.4549570237	-0.9288145723
H	-0.5135684843	2.5347898677	1.2703125833
H	-1.1562183839	0.8204367122	1.2640792987
H	-1.1562183839	0.8204367122	-1.2640792987
H	-0.5135684843	2.5347898677	-1.2703125833
H	0.2836319516	-1.1761641472	0.0000000000
Cl	-0.5585874679	-2.1504104941	0.0000000000

2,5-dihydrofuran···HCl
13
CCSD(T)-F12B/AVTZ+D ENERGY=-691.28466198

O	-0.8270576201	-0.4183548025	0.0000000000
C	-0.8739046694	0.4016328909	1.1812065628
C	-0.8739046694	0.4016328909	-1.1812065628
C	-0.8752204749	1.8088412912	0.6658402130
C	-0.8752204749	1.8088412912	-0.6658402130
H	-0.0002232253	0.1754085909	1.8004221138
H	-1.7762604433	0.1586255292	1.7497414939
H	-1.7762604433	0.1586255292	-1.7497414939
H	-0.0002232253	0.1754085909	-1.8004221138
H	-0.8799090725	2.6754440809	1.3106767600
H	-0.8799090725	2.6754440809	-1.3106767600
H	0.6782990340	-1.2387077335	0.0000000000
Cl	1.9074853572	-1.6880472303	0.0000000000

5.2 B···HCCH

Formaldehyde···HCCH
8
CCSD(T)-F12B/AVTZ+D ENERGY=-191.58968777

C	-1.2724929403	-1.3837450010	0.0000000000
O	-1.7836792136	-0.2881409154	0.0000000000
H	-0.1776076064	-1.5076348674	0.0000000000
H	-1.8816285765	-2.3006477602	0.0000000000
H	0.0535315468	1.0012074674	0.0000000000
C	1.1219151091	1.0193232821	0.0000000000
C	2.3293072244	1.0183064133	0.0000000000
H	3.3925664566	1.0275703807	0.0000000000

Vinyl fluoride···HCCH
10
CCSD(T)-F12B/AVTZ+D ENERGY=-254.84661308

C	-1.1527946736	1.4155184906	0.0000000000
C	-1.8993267553	0.3216020609	0.0000000000
F	-1.3493299596	-0.9110665218	0.0000000000
C	1.9441734470	-0.6887051249	0.0000000000
C	3.0290682751	-0.1600365994	0.0000000000
H	-2.9790942272	0.2807244431	0.0000000000
H	-1.6450549467	2.3761426789	0.0000000000
H	-0.0733013069	1.3660794108	0.0000000000
H	0.9804835989	-1.1423691677	0.0000000000
H	3.9875535483	0.3003103292	0.0000000000

Oxirane···HCCH
11
CCSD(T)-F12B/AVTZ+D ENERGY=-230.81507546

C	-0.0454485820	-1.5013576850	0.7316091939
O	1.0750039321	-0.9855666002	0.0000000000
C	-0.0454485820	-1.5013576850	-0.7316091939
H	0.1517741223	-2.4223265694	1.2661753417
H	-0.6261596717	-0.7514713541	1.2569240280
H	-0.6261596717	-0.7514713541	-1.2569240280
H	0.1517741223	-2.4223265694	-1.2661753417
H	0.6043977004	1.1165453681	0.0000000000
C	-0.1241352622	1.9006200609	0.0000000000
C	-0.9638106762	2.7686302444	0.0000000000
H	-1.6961914309	3.5395641437	0.0000000000

Thiirane···HCCH
11
CCSD(T)-F12B/AVTZ+D ENERGY=-553.44760057

C	-1.1558136034	0.5323479810	0.7412693832
S	-1.1061421828	-1.1268063839	0.0000000000
C	-1.1558136034	0.5323479810	-0.7412693832
H	-2.0789204717	0.7709153537	1.2517280035
H	-0.2453279156	0.8360874497	1.2417863700
H	-0.2453279156	0.8360874497	-1.2417863700
H	-2.0789204717	0.7709153537	-1.2517280035
H	1.5370413464	-0.6199369415	0.0000000000
C	2.2319087101	0.1927660900	0.0000000000
C	2.9963780777	1.1273714831	0.0000000000
H	3.6781840303	1.9435371833	0.0000000000

Methylenecyclopropane···HCCH
14
CCSD(T)-F12B/AVTZ+D ENERGY=-232.93027996

C	-1.2437874195	-0.6968876201	0.7702643833
C	-1.2437874195	-0.6968876201	-0.7702643833
C	-1.1976432059	0.5508948694	0.0000000000
C	-1.1363265288	1.8747565293	0.0000000000
H	-0.3379830269	-1.0317301362	-1.2611148843
H	-2.1674746682	-0.9593850258	-1.2704103283
H	-2.1674746682	-0.9593850258	1.2704103283
H	-0.3379830269	-1.0317301362	1.2611148843
H	-1.1161006623	2.4322694647	0.9284662686
H	-1.1161006623	2.4322694647	-0.9284662686
H	1.4437661388	0.7019306892	0.0000000000
C	2.1871146329	-0.0630008538	0.0000000000
C	3.0155441279	-0.9407247266	0.0000000000
H	3.7495153889	-1.7101878721	0.0000000000

2,5-dihydrofuran···HCCH
15
CCSD(T)-F12B/AVTZ+D ENERGY=-308.12463700
O 0.0000000000 0.1695304378 0.1641894085
C 1.1758848415 0.9854721008 0.1080905332
C -1.1758848415 0.9854721008 0.1080905332
C 0.6658649963 2.3918134227 0.0009162751
C -0.6658649963 2.3918134227 0.0009162751
H 1.7726929105 0.8217594957 1.0110337067
H 1.7785877425 0.6926473312 -0.7590353354
H -1.7726929105 0.8217594957 1.0110337067
H -1.7785877425 0.6926473312 -0.7590353354
H 1.3114386746 3.2555280175 -0.0660911216
H -1.3114386746 3.2555280175 -0.0660911216
H 0.0000000000 -0.8547132039 -1.6547543580
C 0.0000000000 -1.0904848322 -2.6997860795
C 0.0000000000 -1.3449066012 -3.8805751065
H 0.0000000000 -1.5738665363 -4.918901980

5.3 B···ClF

Formaldehyde···ClF
6
CCSD(T)-F12B/AVTZ+D ENERGY=-673.82856355
O -0.9237357422 -1.5820206777 0.0000000000
C -0.0319631582 -2.4012893873 0.0000000000
H 1.0248083243 -2.0960617289 0.0000000000
H -0.2530890728 -3.4775536516 0.0000000000
Cl 0.0090950511 0.7006487032 0.0000000000
F 0.7424835976 2.1755917422 0.0000000000

Vinyl fluoride···ClF
8
CCSD(T)-F12B/AVTZ+D ENERGY=-737.08267759
F 1.1701554196 -1.1270434398 0.0000000000
C 0.5237313224 -2.3145889392 0.0000000000
C -0.7981703764 -2.3830172757 0.0000000000
H 1.2139718338 -3.1454393573 0.0000000000
H -1.2667225618 -3.3552115988 0.0000000000
H -1.4105717303 -1.4930453874 0.0000000000
Cl -0.0517885957 1.2654158112 0.0000000000
F -0.7956393115 2.7204701872 0.0000000000

Oxirane···ClF
9
CCSD(T)-F12B/AVTZ+D ENERGY=-713.05549502
O -0.8901774938 -1.1253244879 0.0000000000
C -0.0176370668 -2.0058521037 0.7317370939
C -0.0176370668 -2.0058521037 -0.7317370939
H 0.7821590547 -1.4997546518 1.2583626585
H -0.5338064496 -2.7920990048 1.2672407785
H 0.7821590547 -1.4997546518 -1.2583626585
H -0.5338064496 -2.7920990048 -1.2672407785
Cl 0.0251472051 1.0746265714 0.0000000000
F 0.7492262120 2.5614684369 0.0000000000

Thiirane···ClF
9
CCSD(T)-F12B/AVTZ+D ENERGY=-1035.69345044
S 1.3441975452 -0.4290048683 0.0000000000
C 1.4292092994 1.2292635659 0.7407555412
C 1.4292092994 1.2292635659 -0.7407555412
H 0.5160372615 1.5117139725 1.2478434962
H 2.3566950759 1.4395846375 1.2553129151
H 0.5160372615 1.5117139725 -1.2478434962
H 2.3566950759 1.4395846375 -1.2553129151
Cl -1.1365254215 -0.5227422038 0.0000000000
F -2.8543463972 -0.4529332793 0.0000000000

Methylenecyclopropane···ClF
12
CCSD(T)-F12B/AVTZ+D ENERGY=-715.17077661
C 1.6551918392 0.8424628440 0.0000000000
C 0.4440193636 1.3958665482 0.0000000000
C -0.6810975465 1.9349459948 0.7700723411
C -0.6810975465 1.9349459948 -0.7700723411
H 2.1667352939 0.6230102250 0.9288341581
H 2.1667352939 0.6230102250 -0.9288341581
H -0.5468504530 2.8847903795 1.2718192624
H -1.3415242289 1.2347543988 1.2655142049
H -0.5468504530 2.8847903795 -1.2718192624
H -1.3415242289 1.2347543988 -1.2655142049
Cl 0.0389999636 -1.2979605010 0.0000000000
F -0.7224132973 -2.7749008875 0.0000000000

2,5-dihydrofuran···ClF
13
CCSD(T)-F12B/AVTZ+D ENERGY=-790.36627416

O	-0.9701607334	0.0643302023	0.0000000000
C	-0.9516809908	0.8865502231	1.1811780124
C	-0.9516809908	0.8865502231	-1.1811780124
C	-0.8035912913	2.2858501217	0.6658799065
C	-0.8035912913	2.2858501217	-0.6658799065
H	-0.1166714826	0.5703579955	1.8123946538
H	-1.8839341440	0.7369565641	1.7341317037
H	-1.8839341440	0.7369565641	-1.7341317037
H	-0.1166714826	0.5703579955	-1.8123946538
H	-0.7183397827	3.1483064008	1.3107422269
H	-0.7183397827	3.1483064008	-1.3107422269
Cl	0.8982246854	-1.3628831688	0.0000000000
F	2.2502074308	-2.3214936438	0.0000000000