Supplementary Material

Proposal of pseudo-intrinsic dynamic nature of interactions: simple methods to generate the perturbed structures and to analyze for the prediction of the nature of high reliability, with the applications

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Table S1. The interaction distances r_o(X, Y) in **1**–**56**, optimized with the MP2/S-TZPsp

Species (No.) (X-*-Y)	r_o(X, Y) (Å)
He-*-HF (**1**)	2.3743
Ne-*-HF (**2**)	2.3724
Ar-*-HF (**3**)	2.5748
Kr-*-HF (**4**)	2.5807
Xe-*-HF (**5**)	2.7654
NN-*-HF (**6**)	2.0557
HF-*-HF (**7**)	1.8323
HCN-*-HF (**8**)	1.8320
H_2O-*-HOH (**9**)	1.9506
Me_2O-*-HOH (**10**)	1.8670
Me_2O-*-Cl_2 (**11**)	2.6165
Me_2O-*-Br_2 (**12**)	2.5901
Me_2O-*-I_2 (**13**)	2.7524
Me_2S-*-Cl_2 (**14**)	2.6339
Me_2S-*-Br_2 (**15**)	2.6735
Me_2S-*-I_2 (**16**)	2.9439
Me_2Se-*-Cl_2 (**17**)	2.5682
Me_2Se-*-Br_2 (**18**)	2.7150
Me_2Se-*-I_2 (**19**)	3.0000
Me_2Te-*-Cl_2 (**20**)	2.5768
Me_2Te-*-Br_2 (**21**)	2.7634
Me_2Te-*-I_2 (**22**)	3.0830
$[Cl\text{-}*\text{-}Cl_2]^-$ (**23**)	2.2976
$[Br\text{-}*\text{-}Br_2]^-$ (**24**)	2.5511
$[I\text{-}*\text{-}I_2]^-$ (**25**)	2.9331
$[Cl\text{-}*\text{-}BrCl]^-$ (**26**)	2.4048
$[Br\text{-}*\text{-}ClBr]^-$ (**27**)	2.4432
$[Cl\text{-}*\text{-}ICl]^-$ (**28**)	2.5568
$[Br\text{-}*\text{-}IBr]^-$ (**29**)	2.7114
Me_2ClS-*-Cl (**30**)	2.2691
Me_2BrS-*-Br (**31**)	2.4411
Me_2ClSe-*-Cl (**32**)	2.3572
Me_2BrSe-*-Br (**33**)	2.5216
Me_2ClTe-*-Cl (**34**)	2.4649
Me_2BrTe-*-Br (**35**)	2.6288
Me_2ITe-*-I (**36**)	2.8721
Me_2S^+-*-Cl (**37**)	1.9862
Me_2S^+-*-Br (**38**)	2.1473
Me_2S^+-*-I (**39**)	2.3643
Me_2Se^+-*-Cl (**40**)	2.1111
Me_2Se^+-*-Br (**41**)	2.2656
Me_2Se^+-*-I (**42**)	2.4789
Me_2Te^+-*-Cl (**43**)	2.2739
Me_2Te^+-*-Br (**44**)	2.4228
Me_2Te^+-*-I (**45**)	2.6372
Cl-*-Cl (**46**)	1.9917
Br-*-Br (**47**)	2.2756
I-*-I (**48**)	2.6545
CH_3-*-Cl (**49**)	1.7780
CH_3-*-Br (**50**)	1.9242
CH_3-*-I (**51**)	2.1196
CH_3-*-CH_3 (**52**)	1.5227
CH_2-*-CH_2 (**53**)	1.3318
CH-*-CH (**54**)	1.2121
CH_3-*-H (**55**)	1.0858
H-*-H (**56**)	0.7383

Table S2. The w'/w ratios for the interactions in **1**–**56**, evaluated with POM-M, POM-Z, and CIV, under the MP2/S-TZPsp condition[a]

Species (No.)	$(w'/w)_{POM-M}$	$(w'/w)_{POM-Z}$	$(w'/w)_{CIV}$	$\Delta(w'/w)_{POM-Z}$[b]	$\Delta(w'/w)_{CIV}$[c]
He-*-H–F (**1**)	0.0000	0.0000	0.0000	0.0000	0.0000
Ne-*-H–F (**2**)	0.0000	-0.0002	-0.0002	0.0002	0.0002
Ar-*-H–F (**3**)	-0.0023	-0.0023	-0.0026	0.0000	0.0004
Kr-*-H–F (**4**)	-0.0047	-0.0047	-0.0051	0.0000	0.0004
Xe-*-H–F (**5**)	-0.0062	-0.0062	-0.0068	0.0000	0.0006
NN-*-H–F (**6**)	-0.0100	-0.0100	-0.0110	0.0000	0.0009
HF-*-H–F (**7**)	-0.0164	-0.0166	-0.0170	0.0002	0.0006
HCN-*-H–F (**8**)	-0.0348	-0.0348	-0.0382	0.0000	0.0034
H_2O-*-H–OH (**9**)	-0.0185	-0.0185	-0.0202	0.0000	0.0017
Me_2O-*-H–OH (**10**)	-0.0308	-0.0308	-0.0259	0.0000	-0.0049
Me_2O-*-Cl–Cl (**11**)	-0.0435	-0.0435	-0.0455	0.0000	0.0021
Me_2O-*-Br–Br (**12**)	-0.0631	-0.0631	-0.0661	0.0000	0.0030
Me_2O-*-I–I (**13**)	-0.0582	-0.0582	-0.0601	0.0000	0.0019
Me_2S-*-Cl–Cl (**14**)	-0.2636	-0.2636	-0.2836	0.0000	0.0200
Me_2S-*-Br–Br (**15**)	-0.2345	-0.2345	-0.2436	0.0000	0.0091
Me_2S-*-I–I (**16**)	-0.1568	-0.1568	-0.1635	0.0000	0.0066
Me_2Se-*-Cl–Cl (**17**)	-0.4229	-0.4231	-0.4276	0.0002	0.0047
Me_2Se-*-Br–Br (**18**)	-0.2742	-0.2742	-0.2799	0.0000	0.0057
Me_2Se-*-I–I (**19**)	-0.1871	-0.1871	-0.1943	0.0000	0.0072
Me_2Te-*-Cl–Cl (**20**)	-0.3209	-0.3211	-0.3022	0.0002	-0.0187
Me_2Te-*-Br–Br (**21**)	-0.3039	-0.3037	-0.2984	-0.0002	-0.0055
Me_2Te-*-I–I (**22**)	-0.2525	-0.2525	-0.2581	0.0000	0.0057
$[Cl$-*-Cl–$Cl]^-$ (**23**)	-0.4084	-0.4084	-0.4250	0.0000	0.0166
$[Br$-*-Br–$Br]^-$ (**24**)	-0.3326	-0.3326	-0.3473	0.0000	0.0147
$[I$-*-I–$I]^-$ (**25**)	-0.3324	-0.3326	-0.3464	0.0002	0.0140
$[Cl$-*-Br–$Cl]^-$ (**26**)	-0.3660	-0.3660	-0.3832	0.0000	0.0172
$[Br$-*-Cl–$Br]^-$ (**27**)	-0.3390	-0.3394	-0.3522	0.0004	0.0132
$[Cl$-*-I–$Cl]^-$ (**28**)	-0.3154	-0.3154	-0.3297	0.0000	0.0144
$[Br$-*-I–$Br]^-$ (**29**)	-0.3109	-0.3108	-0.3245	-0.0001	0.0136
Cl-*-(Me_2)S–Cl (**30**)	-0.3324	-0.3328	-0.3445	0.0004	0.0121
Br-*-(Me_2)S–Br (**31**)	-0.2721	-0.2630	-0.2823	-0.0091	0.0102
Cl-*-(Me_2)Se–Cl (**32**)	-0.2914	-0.2916	-0.3025	0.0002	0.0111
Br-*-(Me_2)Se–Br (**33**)	-0.2623	-0.2623	-0.2725	0.0000	0.0103
Cl-*-(Me_2)Te–Cl (**34**)	-0.1992	-0.1994	-0.2065	0.0002	0.0074
Br-*-(Me_2)Te–Br (**35**)	-0.2058	-0.2060	-0.2134	0.0002	0.0076
I-*-(Me_2)Te–I (**36**)	-0.2194	-0.2196	-0.2279	0.0002	0.0085
$(Me)H_3C$–S^+-*-Cl (**37**)	-0.0147	-0.0147	-0.0136	0.0000	-0.0011
$(Me)H_3C$–S^+-*-Br (**38**)	-0.0128	-0.0128	-0.0119	0.0000	-0.0009
$(Me)H_3C$–S^+-*-I (**39**)	-0.0134	-0.0134	-0.0128	0.0000	-0.0006
$(Me)H_3C$–Se^+-*-Cl (**40**)	-0.0127	-0.0128	-0.0121	0.0002	-0.0006
$(Me)H_3C$–Se^+-*-Br (**41**)	-0.0113	-0.0113	-0.0108	0.0000	-0.0006
$(Me)H_3C$–Se^+-*-I (**42**)	-0.0121	-0.0121	-0.0117	0.0000	-0.0004
$(Me)H_3C$–Te^+-*-Cl (**43**)	-0.0028	-0.0026	-0.0021	-0.0002	-0.0008
$(Me)H_3C$–Te^+-*-Br (**44**)	-0.0023	-0.0023	-0.0017	0.0000	-0.0006
$(Me)H_3C$–Te^+-*-I (**45**)	-0.0047	-0.0047	-0.0042	0.0000	-0.0006
(H_2)H–C-*-Cl (**49**)	-0.0202	-0.0200	-0.0187	-0.0002	-0.0015
(H_2)H–C-*-Br (**50**)	-0.0149	-0.0149	-0.0132	0.0000	-0.0017
(H_2)H–C-*-I (**51**)	-0.0112	-0.0110	-0.0091	-0.0002	-0.0021
H_3C*-C–H(H_2) (**52**)	-0.0180	-0.0180	-0.0176	0.0000	-0.0004
CH_2-*-C–H(H) (**53**)	-0.0140	-0.0140	-0.0144	0.0000	0.0004
CH-*-C–H (**54**)	0.0159	0.0159	0.0151	0.0000	0.0008
(H_2)H–C-*-H (**55**)	-0.0062	-0.0062	-0.0051	0.0000	-0.0011

[a] The w'/w values are calculated when $w = 0.1$ (see eqs. (3) and (4) in the text). [b] $\Delta(w'/w)_{POM-Z} = (w'/w)_{POM-M} - (w'/w)_{POM-Z}$. [c] $\Delta(w'/w)_{CIV} = (w'/w)_{POM-M} - (w'/w)_{CIV}$.

Table S3. QTAIM functions and C_{ii} values for the standard interactions in **1**–**56**, evaluated under the MP2/S-TZPsp condition[a]

Species (X-*-Y) (No: symmetry)	$\rho_b(r_c)$ (au)	$c\nabla^2\rho_b(r_c)$[b] (au)	$H_b(r_c)$ (au)	$k_b(r_c)$[c]	C_{ii}[d] (Å mdyn^{-1})
He-*-HF (**1**: $C_{\infty v}$)	0.0024	0.0018	0.0011	-0.568	210.48
Ne-*-HF (**2**: $C_{\infty v}$)	0.0048	0.0030	0.0011	-0.782	75.94
Ar-*-HF (**3**: $C_{\infty v}$)	0.0074	0.0037	0.0014	-0.764	40.89
Kr-*-HF (**4**: $C_{\infty v}$)	0.0104	0.0043	0.0008	-0.892	21.74
Xe-*-HF (**5**: $C_{\infty v}$)	0.0105	0.0036	0.0006	-0.918	22.13
NN-*-HF (**6**: $C_{\infty v}$)	0.0183	0.0080	0.0008	-0.946	10.07
HF-*-HF (**7**: C_s)	0.0246	0.0124	0.0009	-0.962	6.82
HCN-*-HF (**8**: $C_{\infty v}$)	0.0336	0.0109	-0.0046	-1.175	4.27
H_2O-*-HOH (**9**: C_s)	0.0242	0.0105	0.0004	-0.982	6.71
Me_2O-*-HOH (**10**: C_s)	0.0315	0.0120	-0.0021	-1.079	5.33
Me_2O-*-Cl_2 (**11**: C_s)	0.0240	0.0118	0.0023	-0.894	6.68
Me_2O-*-Br_2 (**12**: C_s)	0.0302	0.0134	0.0013	-0.948	4.54
Me_2O-*-I_2 (**13**: C_s)	0.0280	0.0105	-0.0001	-1.003	4.79
Me_2S-*-Cl_2 (**14**: C_s)	0.0463	0.0108	-0.0060	-1.216	8.25
Me_2S-*-Br_2 (**15**: C_s)	0.0495	0.0100	-0.0078	-1.280	3.17
Me_2S-*-I_2 (**16**: C_s)	0.0372	0.0070	-0.0055	-1.281	3.97
Me_2Se-*-Cl_2 (**17**: C_s)	0.0597	0.0101	-0.0114	-1.362	3.55
Me_2Se-*-Br_2 (**18**: C_s)	0.0516	0.0089	-0.0088	-1.330	2.46
Me_2Se-*-I_2 (**19**: C_s)	0.0384	0.0062	-0.0059	-1.323	3.43
Me_2Te-*-Cl_2 (**20**: C_s)	0.0695	0.0053	-0.0215	-1.670	1.23
Me_2Te-*-Br_2 (**21**: C_s)	0.0578	0.0055	-0.0143	-1.566	1.65
Me_2Te-*-I_2 (**22**: C_s)	0.0416	0.0045	-0.0080	-1.472	2.95
$[Cl\text{-}*\text{-}Cl_2]^-$ (**23**: $D_{\infty h}$)	0.0837	0.0137	-0.0216	-1.441	1.11
$[Br\text{-}*\text{-}Br_2]^-$ (**24**: $D_{\infty h}$)	0.0660	0.0098	-0.0145	-1.425	1.09
$[I\text{-}*\text{-}I_2]^-$ (**25**: $D_{\infty h}$)	0.0508	0.0045	-0.0119	-1.568	1.42
$[Cl\text{-}*\text{-}BrCl]^-$ (**26**: $D_{\infty h}$)	0.0753	0.0114	-0.0201	-1.470	1.03
$[Br\text{-}*\text{-}ClBr]^-$ (**27**: $D_{\infty h}$)	0.0717	0.0117	-0.0158	-1.404	1.12
$[Cl\text{-}*\text{-}ICl]^-$ (**28**: $D_{\infty h}$)	0.0663	0.0079	-0.0212	-1.575	1.02
$[Br\text{-}*\text{-}IBr]^-$ (**29**: $D_{\infty h}$)	0.0590	0.0064	-0.0158	-1.553	1.15
Me_2ClS-*-Cl (**30**: C_2)	0.0964	0.0046	-0.0362	-1.798	0.92
Me_2BrS-*-Br (**31**: C_{2v})	0.0804	0.0058	-0.0238	-1.674	0.98
Me_2ClSe-*-Cl (**32**: C_2)	0.0860	0.0053	-0.0325	-1.756	0.81
Me_2BrSe-*-Br (**33**: C_2)	0.0742	0.0053	-0.0225	-1.680	0.90
Me_2ClTe-*-Cl (**34**: C_2)	0.0779	0.0078	-0.0311	-1.666	0.69
Me_2BrTe-*-Br (**35**: C_2)	0.0695	0.0036	-0.0253	-1.776	0.80
Me_2ITe-*-I (**36**: C_2)	0.0594	0.0013	-0.0191	-1.883	1.02
Me_2S^+-*-Cl (**37**: C_s)	0.1692	-0.0225	-0.1143	-2.649	0.30
Me_2S^+-*-Br (**38**: C_s)	0.1389	-0.0103	-0.0771	-2.363	0.36
Me_2S^+-*-I (**39**: C_s)	0.1071	-0.0012	-0.0541	-2.048	0.44
Me_2Se^+-*-Cl (**40**: C_s)	0.1387	-0.0089	-0.0850	-2.263	0.32
Me_2Se^+-*-Br (**41**: C_s)	0.1190	-0.0065	-0.0603	-2.276	0.38
Me_2Se^+-*-I (**42**: C_s)	0.0967	-0.0032	-0.0444	-2.171	0.46
Me_2Te^+-*-Cl (**43**: C_s)	0.1106	0.0123	-0.0546	-1.690	0.33
Me_2Te^+-*-Br (**44**: C_s)	0.0996	0.0012	-0.0478	-1.951	0.38
Me_2Te^+-*-I (**45**: C_s)	0.0870	-0.0050	-0.0399	-2.335	0.47
Cl-*-Cl (**46**: $D_{\infty h}$)	0.1606	-0.0056	-0.0895	-2.144	0.29
Br-*-Br (**47**: $D_{\infty h}$)	0.1130	-0.0001	-0.0497	-2.005	0.37
I-*-I (**48**: $D_{\infty h}$)	0.0825	-0.0022	-0.0343	-2.149	0.48
CH_3-*-Cl (**49**: C_{3v})	0.1855	-0.0338	-0.1362	-2.987	0.30
CH_3-*-Br (**50**: C_3)	0.1554	-0.0198	-0.0945	-2.724	0.35
CH_3-*-I (**51**: C_{3v})	0.1243	-0.0086	-0.0689	-2.332	0.40
CH_3-*-CH_3 (**52**: D_{3d})	0.2462	-0.0791	-0.2233	-4.431	0.23
CH_2-*-CH_2 (**53**: D_{2h})	0.3545	-0.1527	-0.4608	-3.966	0.11
CH-*-CH (**54**: $D_{\infty h}$)	0.4109	-0.1608	-0.6278	-3.050	0.06
CH_3-*-H (**55**: T_d)	0.2851	-0.1420	-0.3436	-6.761	0.18
H-*-H (**56**: $D_{\infty h}$)	0.2730	-0.1763	-0.3593	-55.617	0.16

[a] Data are given for the interaction in question at the BCP, as shown by He-*-HF, for example. [b] $c\nabla^2\rho_b(r_c) = H_b(r_c) - V_b(r_c)/2$, where $c = \hbar^2/8m$. [c] $k_b(r_c) = V_b(r_c)/G_b(r_c)$. [d] Compliance constants, see eq. (R1) in the main text.

Table S4. Selected structural parameters of the optimized structures for **57a**–**59c**, calculated with MP2/S-TZPsp, together with those observed structures for **57a** and **59a**–**59c**[a]

Species (No.) (^{1}O, ^{1}E, ^{2}E, ^{2}O: symm)	r[b] (Å)	$\Delta r_{calc\text{-}vdW}$[c] (Å)	$\Delta r_{obsd\text{-}calc}$[d] (Å)	θ_1[e] (°)	θ_2[f] (°)	ϕ_1[g] (°)	ϕ_2[h] (°)	ϕ_3[i] (°)	ϕ_4[j] (°)	Type[k]
57a (S, S: C_2)	2.9072	-0.6928	0.0196[l]	121.7	121.7	-155.3	-155.3			**CC**
57a (S, S: C_1)	2.9995	-0.6005	*m*	124.0	121.6	-69.6	-171.9			**AB**
57b (O, S, S: C_1)	3.0712	-0.5288	*m*	122.5	126.9	-70.6	-72.5	-178.7		**AA**
57c (O, S, S, O: C_2)	3.0950	-0.5051	*m*	124.8	124.8	72.0	72.0	175.9	175.9	**AA**
58a (S, Se: C_1)	3.0134	-0.6866	*m*	122.9	122.7	70.5	168.8			**AB**
58b (S, Se, O: C_1)	3.0732	-0.6268	*m*	121.6	127.7	72.6	72.4		174.7	**AA**
58b' (O, S, Se: C_1)	3.1551	-0.5449	*m*	127.0	123.5	71.4	66.2	177.6		**AA**
58c (O, S, Se, O: C_1)	3.1317	-0.5683	*m*	123.2	126.9	77.6	74.1	-173.8	177.5	**AA**
59a (Se, Se: C_2)	3.0410	-0.7590	0.0167[l]	122.8	122.8	-133.8	-133.8			**CC**
59a (Se, Se: C_1)	3.1043	-0.6957	*m*	123.6	122.9	-65.2	-164.9			**AB**
59b (O, Se, Se: C_1)	3.1565	-0.6435	0.0021	122.3	128.1	-68.3	-71.0	-173.3		**AA**
59c (O, Se, Se, O: C_2)	3.1970	-0.6030	-0.0458	125.7	125.7	-74.4	-74.4	-178.5	-178.5	**AA**
57a (S, S: C_1)$_{obsd\text{-}A}$[n]	2.9181	-0.6819		121.1	122.5	-158.3	-143.3			**CC**
57a (S, S: C_1)$_{obsd\text{-}B}$[n]	2.9356	-0.6644		122.1	123.5	-142.1	-153.0			**CC**
59a (Se, Se: C_1)$_{obsd\text{-}A}$[n]	3.0513	-0.6487		123.9	122.9	-138.8	-154.1			**CC**
59a (Se, Se: C_1)$_{obsd\text{-}B}$[n]	3.0642	-0.7358		123.2	123.0	136.8	148.1			**CC**
59b (O, Se, Se: C_1)$_{obsd}$	3.1586	-0.6414		124.2	126.9	84.6	82.9		-175.0	**AA**
59c (O, Se, Se, O: C_1)$_{obsd}$	3.1512	-0.6488		124.7	124.3	-87.1	-86.5	169.5	169.2	**AA**

[a] See Scheme S1 for definition of selected structural parameters. [b] Distances between ^{1}E and ^{2}E atoms. [c] $\Delta r_{obsd\text{-}calc} = r_{obsd} - r_{calc}$, where r_{obsd} and r_{calc} are observed and calculated distances for ^{1}E···^{2}E, respectively. [d] $\Delta r_{calc\text{-}vdW} = r_{calc} - \Sigma r_{vdW}$, where r_{obsd} and r_{vdW} are observed distances and van der Waals radii (A. Bondi, *J. Phys. Chem.*, **1964**, *68*, 441–451.) for ^{1}E and ^{2}E, respectively. [e] $\angle C_{8a}C_1{}^1E$. [f] $\angle C_{8a}C_8{}^2E$. [g] $\phi(C_{8a}C_1{}^1E{}^1C_{Me})$. [h] $\phi(C_{8a}C_8{}^2E{}^2C_{Me})$. [i] $\phi(C_{8a}C_1{}^1E{}^1O)$. [j] $\phi(C_{8a}C_8{}^2E{}^2O)$. [k] See Scheme S1 for definition of types. [l] Averaged values were calculated for r_{obsd}. [m] No X-ray crystal structure. [n] Two structures were obtained by X-ray crystallography.

Table S5. QTAIM functions and QTAIM-DFA parameters of $\rho_b(\boldsymbol{r}_c)$, $\nabla^2\rho_b(\boldsymbol{r}_c)$, $H_b(\boldsymbol{r}_c)$, $k_b(\boldsymbol{r}_c)$, $\kappa_{p:POM\text{-}M}$, and $\kappa_{p:CIV}$ for **57a**–**59c**, together with C_{ii} values, evaluated under the MP2/S-TZPsp condition[a]

Species (X-*-Y) (No: type (symm))	$\rho_b(\boldsymbol{r}_c)$ (au)	$\nabla^2\rho_b(\boldsymbol{r}_c)$[b] (au)	$H_b(\boldsymbol{r}_c)$ (au)	$k_b(\boldsymbol{r}_c)$[c]	$\kappa_{p:POM\text{-}M}$[d] (au^{-1})	$\kappa_{p:CIV}$[d] (au^{-1})	C_{ii}[e] (Å mdyn^{-1})
S-*-S (**57a**: **CC** (C_2))	0.0231	0.0079	-0.0004	-1.027	107.8	89.6	1.932
S-*-S (**57a**: **AB** (C_1))	0.0231	0.0070	-0.0007	-1.046	*f*	100.3	2.210
S-*-S=O (**57b**: **AA** (C_1))	0.0213	0.0062	-0.0006	-1.049	106.4	105.3	2.565
O=S-*-S=O (**57c**: **AA**(C_2))	0.0184	0.0058	-0.0001	-1.012	107.6	104.9	2.576
S-*-Se (**58a**: **AB** (C_1))	0.0252	0.0071	-0.0012	-1.076	121.6	118.5	2.251
S-*-Se=O (**58b**: **AA** (C_1))	0.0236	0.0063	-0.0011	-1.080	127.1	126.9	2.512
Se-*-S=O (**58b'**: **AA** (C_1))	0.0208	0.0056	-0.0008	-1.063	113.7	111.4	2.548
O=S-*-Se=O (**58c**: **AA** (C_1))	0.0192	0.0057	-0.0003	-1.026	124.7	127.8	2.641
Se-*-Se (**59a**: **CC** (C_2))	0.0242	0.0069	-0.0009	-1.060	167.3	129.9	2.431
Se-*-Se (**59a**: **AB** (C_1))	0.0242	0.0063	-0.0012	-1.086	*f*	125.6	2.280
Se-*-Se=O (**59b**: **AA** (C_1))	0.0232	0.0056	-0.0013	-1.100	134.6	133.1	2.518
O=Se-*-Se=O (**59c**: **AA** (C_2))	0.0186	0.0052	-0.0004	-1.037	132.6	131.7	2.663

[a] Data are given for the interaction in question at the BCP, as shown by S-*-S, for example. [b] $c\nabla^2\rho_b(\boldsymbol{r}_c) = H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$, where $c = \hbar^2/8m$. [c] $k_b(\boldsymbol{r}_c) = V_b(\boldsymbol{r}_c)/G_b(\boldsymbol{r}_c)$. [d] $\kappa_p = |\,d^2y/dx^2|\,/[1 + (dy/dx)^2]^{3/2}$. [e] Compliance constants, see eq. (R1) in the main text. [f] Not calculated.

Table S6. Contributions from the donor-acceptor (NBO(*i*)→NBO(*j*)) interactions in the optimized structures for **57a**–**59c**, evaluated with the NBO6 analysis under the M06-2X/S-TZPsp//MP2/S-TZPsp condition

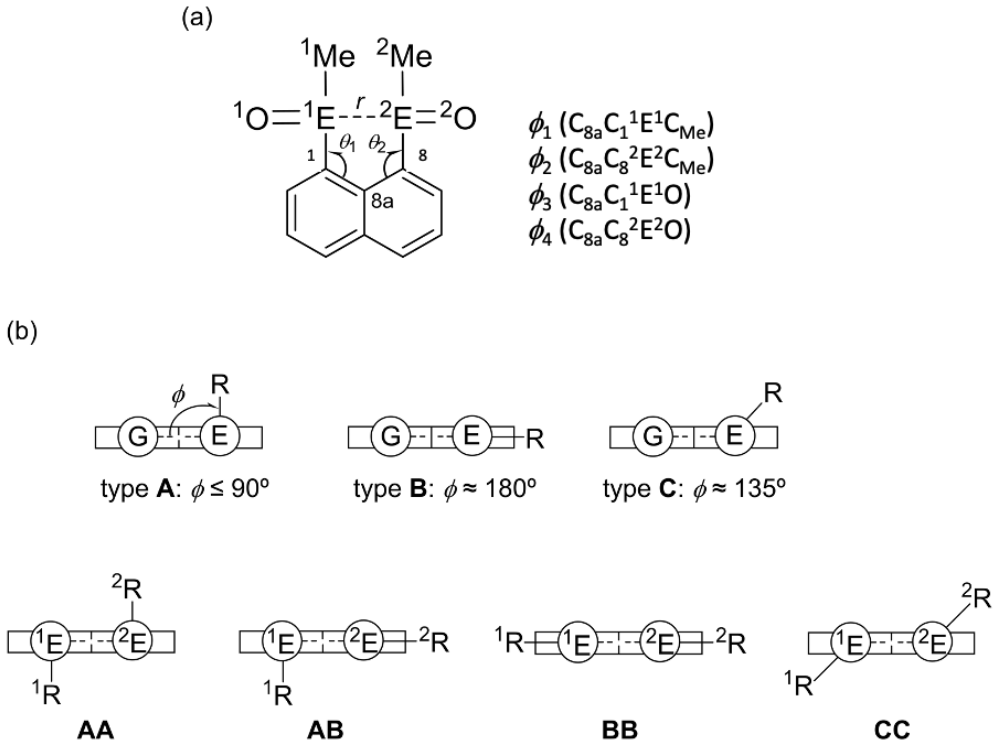
Species (X-*-Y) (No: type (symm))	NBO(*i*)→NBO(*j*)	$E(2)^a$ (kcal mol^{-1})	ΔE^b (au)	$F(i,j)^c$ (au)
S-*-S (**57a**: **CC** (C_2))	n_s(S)→σ*(S−C_{Me})	2.85[d]	0.89	0.045
	n_p(S)→σ*(S−C_{Me})	0.55[d]	0.50	0.015
S-*-S (**57a**: **AB** (C_1))	n_p(S)→σ*(S−C_{Me})	5.71	0.50	0.048
S-*-S=O (**57b**: C_1)	n_p(S)→σ*(S=O)	3.36	0.65	0.042
O=S-*-S=O (**57c**: C_2)	n_s(S)→σ*(S=O)	1.30[d]	0.95	0.031
S-*-Se (**58a**: **AB** (C_1))	n_p(S)→σ*(Se−C_{Me})	9.04	0.46	0.058
S-*-Se=O (**58b**: C_1)	n_p(S)→σ*(Se=O)	5.54	0.56	0.050
Se-*-S=O (**58b'**: C_1)	n_p(Se)→σ*(S=O)	3.56	0.64	0.042
O=S-*-Se=O (**58c**: C_1)	n_s(S)→σ*(Se=O)	2.27	0.85	0.039
	n_s(Se)→σ*(S=O)	1.02	1.02	0.029
Se-*-Se (**59a**: **CC** (C_2))	n_s(Se)→σ*(Se−C_{Me})	2.53[d]	0.90	0.043
	n_p(Se)→σ*(Se−C_{Me})	3.35[d]	0.44	0.034
Se-*-Se (**59a**: **AB** (C_1))	n_s(Se)→σ*(Se−C_{Me})	0.73	0.90	0.023
	n_p(Se)→σ*(Se−C_{Me})	9.86	0.44	0.059
Se-*-Se=O (**59b**: C_1)	n_p(Se)→σ*(Se=O)	6.18	0.54	0.052
O=Se-*-Se=O (**59c**: C_2)	n_s(Se)→σ*(Se=O)	1.73[d]	0.92	0.035

[a] Second-perturbation energy. [b] The diagonal elements (orbital energies). [c] The off-diagonal NBO Fock matrix element. [d] Only one side of the CT interaction is shown due to C_2 symmetry.

Table S7. Torsion angles for φ_1 and φ_2 of the perturbed structures (w = 0.05) generated with CIV and OMA for **57a**–**59c**, and the differences for $\Delta\varphi_{1:CIV–OMA}$ and $\Delta\varphi_{2:CIV–OMA}$, evaluated with MP2/S-TZPsp, together with force constants corresponding to torsion-vibrations for f_1 and f_2, calculated with frequency analysis[a]

Species (X-*-Y) (No: type (symm))	$\varphi_{1:CIV}$[b] (º)	$\varphi_{2:CIV}$[c] (º)	$\varphi_{1:OMA}$[d] (º)	$\varphi_{2:OMA}$[e] (º)	$\Delta\varphi_{1:CIV–OMA}$[f] (º)	$\Delta\varphi_{2:CIV–OMA}$[g] (º)
S-*-S (**57a**: **CC** (C_2))	-154.2	-154.2	-155.2	-155.2	1.0	1.0
S-*-S (**57a**: **AB** (C_1))	-68.7	-171.7	-69.5	-171.8	0.8	0.2
S-*-S=O (**57b**: **AA** (C_1))	-70.0	-72.2	-70.4	-72.4	0.4	0.2
O=S-*-S=O (**57c**: **AA**(C_2))	-75.8	-75.8	-76.2	-76.2	0.4	0.4
S-*-Se (**58a**: **AB** (C_1))	69.7	168.4	70.3	168.7	-0.7	-0.3
S-*-Se=O (**58b**: **AA** (C_1))	72.1	72.1	72.5	72.3	-0.4	-0.2
Se-*-S=O (**58b'**: **AA** (C_1))	71.0	65.6	71.3	66.1	-0.3	-0.5
O=S-*-Se=O (**58c**: **AA** (C_1))	77.2	73.7	77.6	74.0	-0.4	-0.3
Se-*-Se (**59a**: **CC** (C_2))	-132.6	-132.6	-133.7	-133.7	1.1	1.1
Se-*-Se (**59a**: **AB** (C_1))	-64.3	-164.6	-65.0	-164.8	0.7	0.2
Se-*-Se=O (**59b**: **AA** (C_1))	-67.8	-70.8	-68.2	-71.0	0.4	0.2
O=Se-*-Se=O (**59c**: **AA** (C_2))	-74.0	-74.0	-74.3	-74.3	0.3	0.3

[a] See Scheme S1 for definition of φ_1 and φ_2. [b] $\varphi(C_{8a}C_8{}^1E^1C_{Me})$ in perturbed structures generated with CIV method. [c] $\varphi(C_{8a}C_1{}^2E^2C_{Me})$ in perturbed structures generated with CIV method. [d] $\varphi(C_{8a}C_1{}^1E^1C_{Me})$ in perturbed structures generated with OMA method. [e] $\varphi(C_{8a}C_1{}^2E^2C_{Me})$ in perturbed structures generated with OMA method. [f] $\Delta\varphi_{1:CIV–OMA} = \varphi_{1:CIV} - \varphi_{1:OMA}$. [g] $\Delta\varphi_{2:CIV–OMA} = \varphi_{2:CIV} - \varphi_{2:OMA}$.



Scheme S1. Definition of selected structural parameters (a) and types for **A**, **B**, and **C**, together with **AA**, **AB**, **BB**, and **CC** (b).

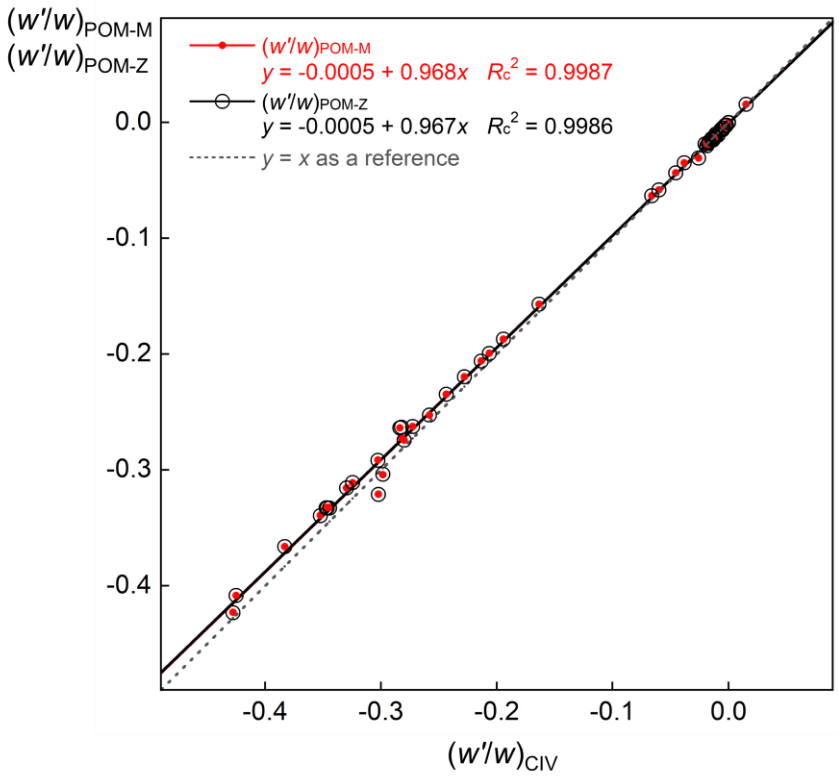


Figure S1. Plots of $(w'/w)_{POM-M}$ and $(w'/w)_{POM-Z}$ versus $(w'/w)_{CIV}$ for **1**–**56**, except for diatomic molecules of **46**–**48** and **56**, evaluated with MP2/S-TZPsp. The correlations are shown in the figure.

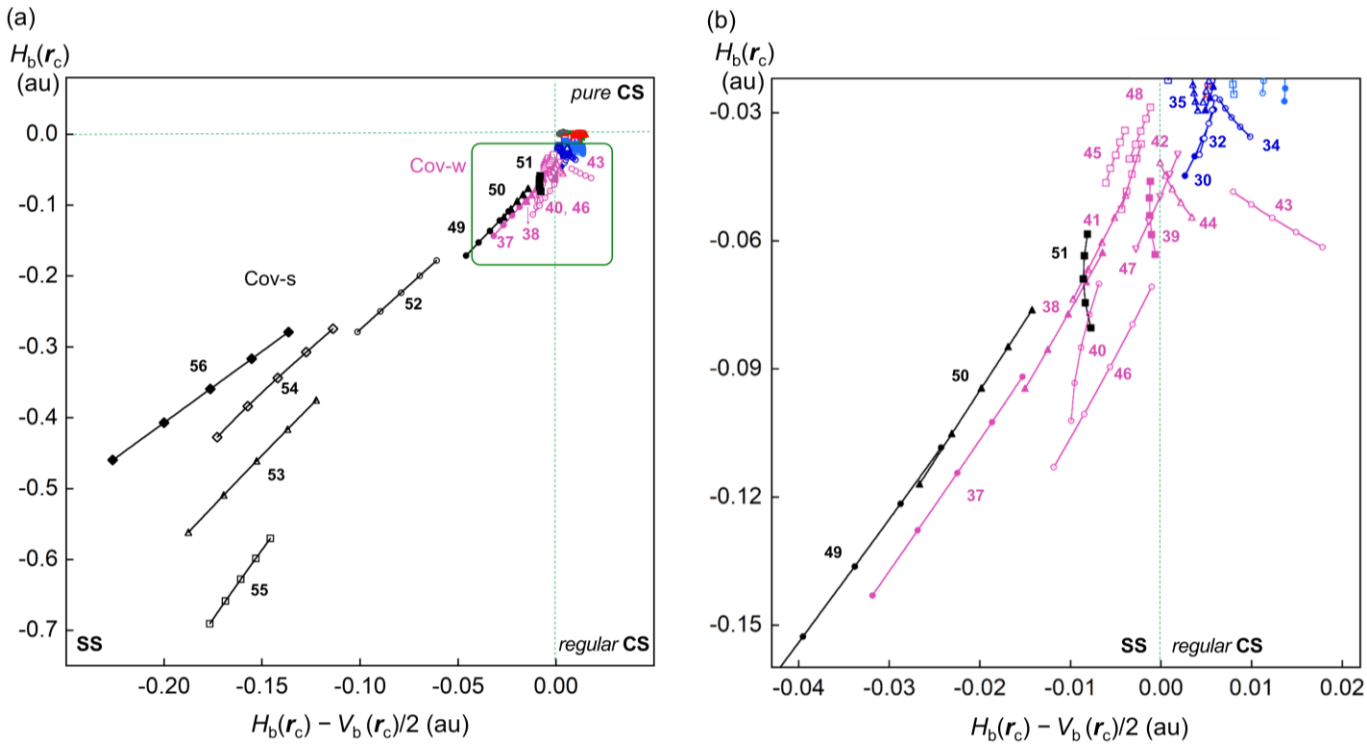


Figure S2. QTAIM-DFA plots of $H_b(r_c)$ versus $H_b(r_c) - V_b(r_c)/2$ for **1**–**56**, together with the perturbed structures generated employing POM-M under the MP2/S-TZPsp condition. Whole picture of the plots (a) and the partial one for **37**–**49** (b). The numbers and colors in the figure are the same as those in Table 3 in the text.

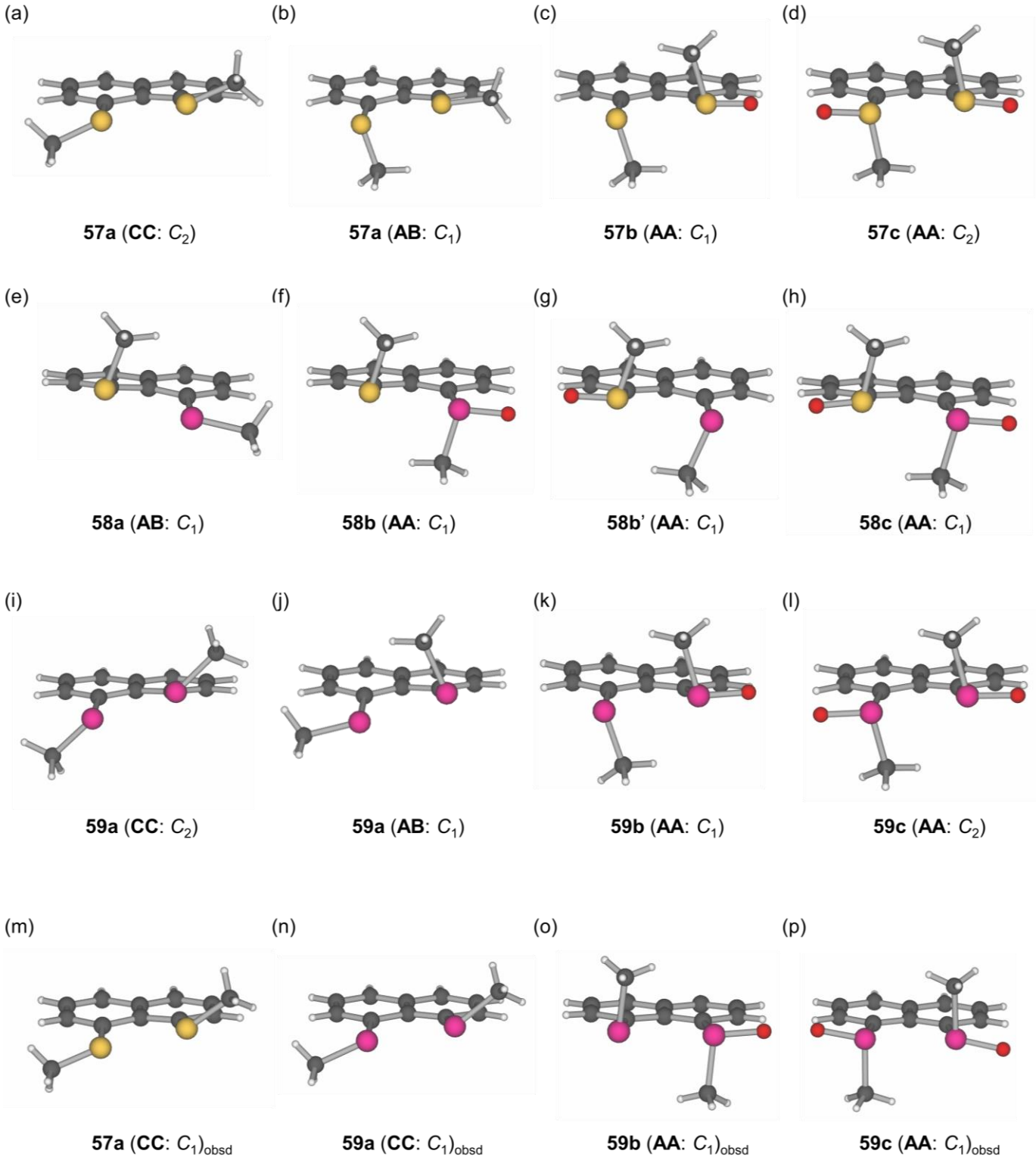


Figure S3. Top views of optimized structures for **57a**–**59c**, (a)–(l), respectively, evaluated by MP2/S-TZPsp, together with observed structures for **57a** (m), **59a** (n), **59b** (o), and **59c** (p). Carbon, hydrogen, selenium, sulfur, and oxygen atoms are shown in black, grey, pink, yellow, and red, respectively.

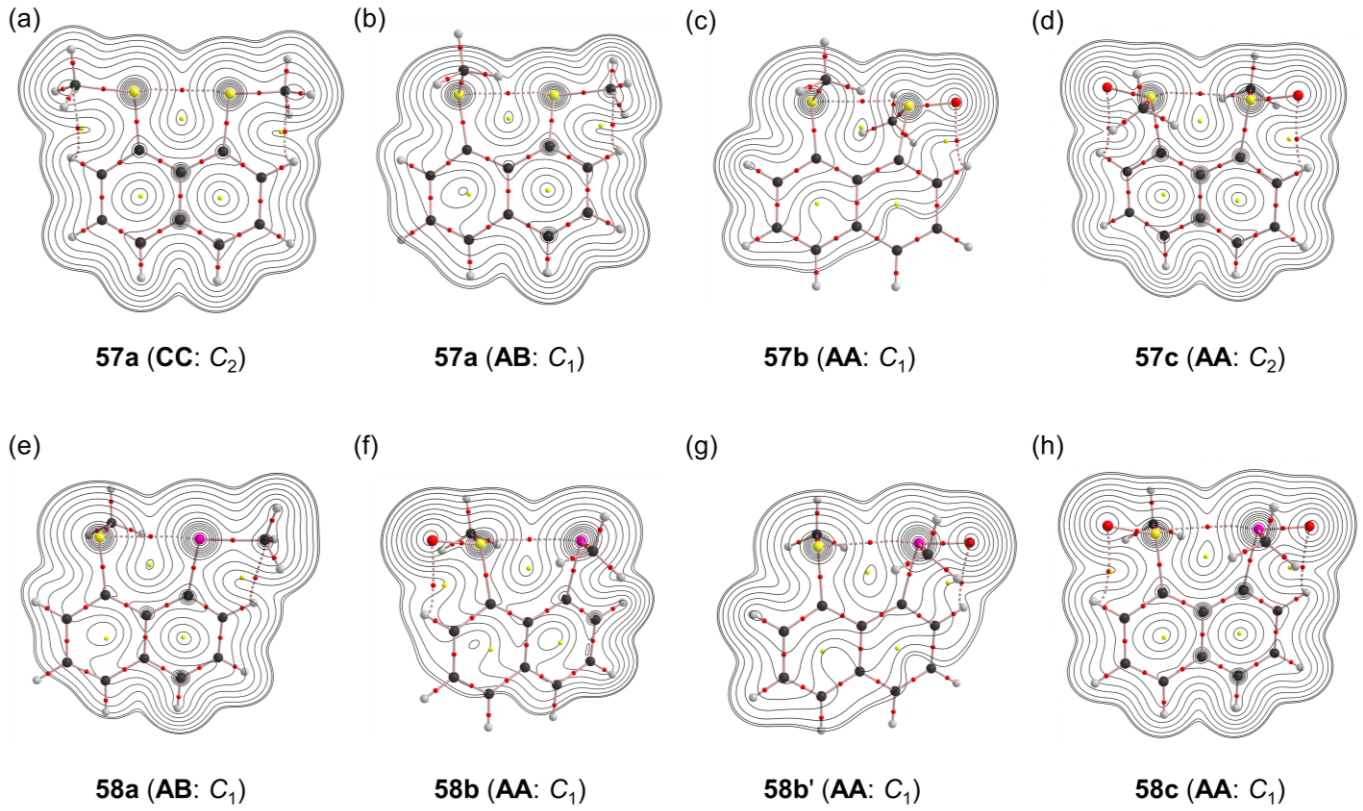


Figure S4. Molecular graphs for **57a**–**58c**, (a)–(h), respectively, evaluated with MP2/S-TZPsp. BCPs are denoted by red dots, RCP (ring critical points) by yellow dots and BPs by pink lines. Carbon, hydrogen, selenium, sulfur, and oxygen atoms are shown in black, grey, pink, yellow, and red, respectively. Contour plots are drawn on the planes containing ^{1}E-*-^{2}E interaction. The contours (ea_o^{-3}) are at 2^l (l = ±8, ±7, ... and 0).

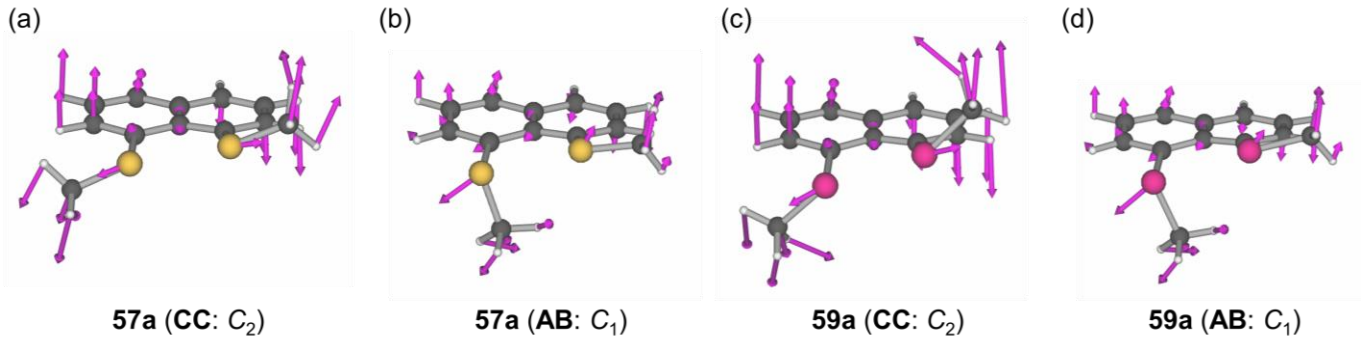


Figure S5. The vibrational motions of CIV corresponding to ^{1}E-*-^{2}E for **57a** (**CC**: C_2) (a), **59a** (**CC**: C_2) (b), **57a** (**AB**: C_1) (c), and **59a** (**AB**: C_1) (d). Carbon, hydrogen, selenium, and sulfur atoms are shown in black, grey, pink, and yellow, respectively.

Optimized structures given by Cartesian coordinates

Optimized structures given by Cartesian coordinates for examined molecules, together with the total energies, evaluated with MP2/S-TZPsp method of the Gaussian 09 program. S-TZPsp shows Sapporo-TZP with 1s1p diffuse functions. The optimized structures were confirmed by the frequency analysis.

MP2/S-TZPsp
Adduct **1**: He-*-HF
Symmetry $C_{\infty v}$
Energy MP2 = –103.220068 au
Standard orientation

10	0	0.000000	0.000000	1.599904
1	0	0.000000	0.000000	-0.772525
9	0	0.000000	0.000000	-1.691835

MP2/S-TZPsp
Adduct **2**: Ne-*-HF
Symmetry $C_{\infty v}$
Energy MP2 = –229.111890 au
Standard orientation

2	0	0.000000	0.000000	-2.667995
1	0	0.000000	0.000000	-0.293722
9	0	0.000000	0.000000	0.625523

MP2/S-TZPsp
Adduct **3**: Ar-*-HF
Symmetry $C_{\infty v}$
Energy MP2 = –627.295719 au
Standard orientation

1	0	0.000000	0.000000	-1.359486
9	0	0.000000	0.000000	-2.279543
18	0	0.000000	0.000000	1.215298

MP2/S-TZPsp
Adduct **4**: Kr-*-HF
Symmetry $C_{\infty v}$
Energy MP2 = –2852.552550 au
Standard orientation

1	0	0.000000	0.000000	-1.839486
9	0	0.000000	0.000000	-2.760420
36	0	0.000000	0.000000	0.741202

MP2/S-TZPsp
Adduct **5**: Xe-*-HF
Symmetry $C_{\infty v}$
Energy MP2 = –7332.547900 au
Standard orientation

1	0	0.000000	0.000000	-2.203689
9	0	0.000000	0.000000	-3.125327
54	0	0.000000	0.000000	0.561697

MP2/S-TZPsp

Adduct **6**: NN-*-HF
Symmetry $C_{\infty v}$
Energy MP2 = –209.676844 au
Standard orientation

7	0	0.000000	0.000000	-1.989923
7	0	0.000000	0.000000	-0.878371
1	0	0.000000	0.000000	1.177311
9	0	0.000000	0.000000	2.100083

MP2/S-TZPsp
Adduct **7**: HF-*-HF
Symmetry C_s
Energy MP2 = –200.657490 au
Standard orientation

9	0	0.037556	-1.311032	0.000000
1	0	0.140306	0.518420	0.000000
1	0	-0.816309	-1.659736	0.000000
9	0	0.037556	1.437845	0.000000

MP2/S-TZPsp
Adduct **8**: HCN-*-HF
Symmetry $C_{\infty v}$
Energy MP2 = –193.582601 au
Standard orientation

1	0	0.000000	0.000000	-2.957857
6	0	0.000000	0.000000	-1.891791
7	0	0.000000	0.000000	-0.729577
1	0	0.000000	0.000000	1.102457
9	0	0.000000	0.000000	2.034799

MP2/S-TZPsp
Adduct **9**: H_2O-*-HOH
Symmetry C_s
Energy MP2 = –152.642453 au
Standard orientation

8	0	0.001974	-1.389014	0.000000
1	0	0.476750	-1.734682	0.759799
1	0	0.476750	-1.734682	-0.759799
1	0	-0.083715	0.559654	0.000000
8	0	0.001974	1.522363	0.000000
1	0	-0.901361	1.842917	0.000000

MP2/S-TZPsp
Adduct **10**: Me_2O-*-HOH
Symmetry C_s
Energy MP2 = –231.040265 au
Standard orientation

8	0	0.701098	-0.125503	0.000000
6	0	0.701098	0.678230	1.167755
1	0	0.702845	0.008637	2.022303
1	0	-0.190402	1.309778	1.204848
1	0	1.591144	1.311599	1.198935
6	0	0.701098	0.678230	-1.167755
1	0	0.702845	0.008637	-2.022303
1	0	1.591144	1.311599	-1.198935

1	0	-0.190402	1.309778	-1.204848
1	0	-0.957924	-0.981816	0.000000
8	0	-1.911392	-1.161862	0.000000
1	0	-1.980074	-2.118041	0.000000

MP2/S-TZPsp
Adduct **11**: Me_2O-*-Cl_2
Symmetry C_s
Energy MP2 = –1074.011895 au
Standard orientation

8	0	1.840253	0.645067	0.000000
6	0	1.840253	1.446229	1.166315
1	0	1.830284	0.775279	2.020028
1	0	0.954392	2.087541	1.198771
1	0	2.734836	2.073754	1.206000
6	0	1.840253	1.446229	-1.166315
1	0	1.830284	0.775279	-2.020028
1	0	0.954392	2.087541	-1.198771
1	0	2.734836	2.073754	-1.206000
17	0	-0.486063	-0.552501	0.000000
17	0	-2.328295	-1.352701	0.000000

MP2/S-TZPsp
Adduct **12**: Me_2O-*-Br_2
Symmetry C_s
Energy MP2 = –5299.973555 au
Standard orientation

8	0	0.476064	2.612045	0.000000
6	0	-0.182649	3.069801	1.169085
1	0	0.361569	2.673965	2.021000
1	0	-1.214759	2.709436	1.197405
1	0	-0.181281	4.161827	1.207424
6	0	-0.182649	3.069801	-1.169085
1	0	0.361569	2.673965	-2.021000
1	0	-1.214759	2.709436	-1.197405
1	0	-0.181281	4.161827	-1.207424
35	0	0.195570	0.037229	0.000000
35	0	-0.182649	-2.232212	0.000000

MP2/S-TZPsp
Adduct **13**: Me_2O-*-I_2
Symmetry C_s
Energy MP2 = –13990.880692 au
Standard orientation

8	0	0.461640	3.196548	0.000000
6	0	-0.194399	3.659010	1.169747
1	0	0.348414	3.261295	2.021783
1	0	-1.228063	3.303224	1.199300
1	0	-0.187068	4.750804	1.206398
6	0	-0.194399	3.659010	-1.169747
1	0	0.348414	3.261295	-2.021783
1	0	-1.228063	3.303224	-1.199300
1	0	-0.187068	4.750804	-1.206398
53	0	0.208986	0.455754	0.000000
53	0	-0.194399	-2.193700	0.000000

MP2/S-TZPsp
Adduct **14**: Me_2S-*-Cl_2
Symmetry C_s
Energy MP2 = –1396.599605 au
Standard orientation

16	0	1.833594	-0.216889	0.000000
6	0	1.833594	0.953834	1.365625
1	0	1.765870	0.378276	2.285560
1	0	0.968511	1.610047	1.287537
1	0	2.754263	1.533879	1.367248
6	0	1.833594	0.953834	-1.365625
1	0	1.765870	0.378276	-2.285560
1	0	2.754263	1.533879	-1.367248
1	0	0.968511	1.610047	-1.287537
17	0	-0.789859	-0.451018	0.000000
17	0	-2.875902	-0.432522	0.000000

MP2/S-TZPsp
Adduct **15**: Me_2S-*-Br_2
Symmetry C_s
Energy MP2 = –5622.563500 au
Standard orientation

16	0	0.742054	2.479586	0.000000
6	0	-0.375339	2.822216	1.367335
1	0	0.145337	2.554702	2.283473
1	0	-1.269481	2.209302	1.269064
1	0	-0.632695	3.879173	1.387445
6	0	-0.375339	2.822216	-1.367335
1	0	0.145337	2.554702	-2.283473
1	0	-0.632695	3.879173	-1.387445
1	0	-1.269481	2.209302	-1.269064
35	0	0.265192	-0.151074	0.000000
35	0	-0.375339	-2.443963	0.000000

MP2/S-TZPsp
Adduct **16**: Me_2S-*-I_2
Symmetry C_s
Energy MP2 = –14313.468910 au
Standard orientation

16	0	3.218977	0.000000	-0.451772
6	0	3.405362	-1.366147	0.705681
1	0	3.216035	-2.284634	0.155410
1	0	2.674892	-1.271726	1.507662
1	0	4.415689	-1.384298	1.109034
6	0	3.405354	1.366155	0.705673
1	0	3.216016	2.284637	0.155398
1	0	2.674888	1.271732	1.507658
1	0	4.415683	1.384318	1.109022
53	0	0.279791	-0.000003	-0.285954
53	0	-2.411510	0.000001	0.157955

MP2/S-TZPsp
Adduct **17**: Me_2Se-*-Cl_2
Symmetry C_s
Energy MP2 = –3398.974601 au
Standard orientation

34	0	1.442294	-0.250326	0.000000
6	0	1.442294	1.029597	1.438229
1	0	1.340499	0.472329	2.365293
1	0	0.587838	1.689367	1.310741
1	0	2.375780	1.585835	1.438445
6	0	1.442294	1.029597	-1.438229
1	0	1.340499	0.472329	-2.365293
1	0	2.375780	1.585835	-1.438445
1	0	0.587838	1.689367	-1.310741
17	0	-1.122592	-0.380769	0.000000
17	0	-3.286453	-0.286238	0.000000

MP2/S-TZPsp
Adduct **18**: Me_2Se-*-Br_2
Symmetry C_s
Energy MP2 = –7624.938422 au
Standard orientation

34	0	2.247092	-0.146763	0.000000
6	0	2.247092	1.135485	1.438207
1	0	2.117242	0.580815	2.363363
1	0	1.408060	1.812039	1.296662
1	0	3.190809	1.673739	1.455025
6	0	2.247092	1.135485	-1.438207
1	0	2.117242	0.580815	-2.363363
1	0	3.190809	1.673739	-1.455025
1	0	1.408060	1.812039	-1.296662
35	0	-0.463944	-0.292873	0.000000
35	0	-2.873155	-0.186244	0.000000

MP2/S-TZPsp
Adduct **19**: Me_2Se-*-I_2
Symmetry C_s
Energy MP2 = –16315.842970 au
Standard orientation

34	0	0.743209	2.839002	0.000000
6	0	-0.517738	3.095680	1.436978
1	0	-0.002464	2.861377	2.364500
1	0	-1.350056	2.409427	1.299902
1	0	-0.858551	4.127220	1.451941
6	0	-0.517738	3.095680	-1.436978
1	0	-0.002464	2.861377	-2.364500
1	0	-1.350056	2.409427	-1.299902
1	0	-0.858551	4.127220	-1.451941
53	0	0.241623	-0.118784	0.000000
53	0	-0.517738	-2.758014	0.000000

MP2/S-TZPsp
Adduct **20**: Me_2Te-*-Cl_2
Symmetry C_s
Energy MP2 = –7610.799173 au
Standard orientation

52	0	0.581606	1.112511	0.000000
6	0	-0.820407	1.422875	1.546818
1	0	-0.344960	1.167052	2.489723
1	0	-1.653145	0.748805	1.362025
1	0	-1.141687	2.460349	1.560754

6	0	-0.820407	1.422875	-1.546818
1	0	-0.344960	1.167052	-2.489723
1	0	-1.653145	0.748805	-1.362025
1	0	-1.141687	2.460349	-1.560754
17	0	-0.010127	-1.395400	0.000000
17	0	-0.820407	-3.526805	0.000000

MP2/S-TZPsp
Adduct **21**: Me_2Te-*-Br_2
Symmetry C_s
Energy MP2 = –11836.761014 au
Standard orientation

52	0	1.997015	-0.305830	0.000000
6	0	1.997015	1.135285	1.546692
1	0	1.823023	0.619406	2.486998
1	0	1.175267	1.818950	1.349222
1	0	2.949585	1.655830	1.577603
6	0	1.997015	1.135285	-1.546692
1	0	1.823023	0.619406	-2.486998
1	0	1.175267	1.818950	-1.349222
1	0	2.949585	1.655830	-1.577603
35	0	-0.766009	-0.260834	0.000000
35	0	-3.225554	0.092015	0.000000

MP2/S-TZPsp
Adduct **22**: Me_2Te-*-I_2
Symmetry C_s
Energy MP2 = –20527.663233 au
Standard orientation

52	0	2.680395	-0.410890	0.000000
6	0	2.680395	1.037474	1.545982
1	0	2.496666	0.526219	2.487015
1	0	1.867008	1.730490	1.346113
1	0	3.636740	1.550228	1.582024
6	0	2.680395	1.037474	-1.545982
1	0	2.496666	0.526219	-2.487015
1	0	1.867008	1.730490	-1.346113
1	0	3.636740	1.550228	-1.582024
53	0	-0.398404	-0.250183	0.000000
53	0	-3.140202	0.274762	0.000000

MP2/S-TZPsp
Adduct **23**: $[Cl$-*-$Cl_2]^-$
Symmetry $D_{\infty h}$
Energy MP2 = –1379.062461 au
Standard orientation

17	0	0.000000	0.000000	0.000000
17	0	0.000000	0.000000	2.297638
17	0	0.000000	0.000000	-2.297638

MP2/S-TZPsp
Adduct **24**: $[Br$-*-$Br_2]^-$
Symmetry $D_{\infty h}$
Energy MP2 = –7718.005333 au
Standard orientation

35	0	0.000000	0.000000	0.000000
35	0	0.000000	0.000000	2.551093
35	0	0.000000	0.000000	-2.551093

MP2/S-TZPsp
Adduct **25**: $[I\text{-}*\text{-}I_2]^-$
Symmetry $D_{\infty h}$
Energy MP2 = –20754.360296 au

53	0	0.000000	0.000000	0.000000
53	0	0.000000	0.000000	2.933051
53	0	0.000000	0.000000	-2.933051

MP2/S-TZPsp
Adduct **26**: $[Cl\text{-}*\text{-}BrCl]^-$
Symmetry $D_{\infty h}$
Energy MP2 = –3492.054993 au

35	0	0.000000	0.000000	0.000000
17	0	0.000000	0.000000	2.404824
17	0	0.000000	0.000000	-2.404824

MP2/S-TZPsp
Adduct **27**: $[Br\text{-}*\text{-}ClBr]^-$
Symmetry $D_{\infty h}$
Energy MP2 = –5605.015886 au

17	0	0.000000	0.000000	0.000000
35	0	0.000000	0.000000	2.443204
35	0	0.000000	0.000000	-2.443204

MP2/S-TZPsp
Adduct **28**: $[Cl\text{-}*\text{-}ICl]^-$
Symmetry $D_{\infty h}$
Energy MP2 = –7837.522556 au

53	0	0.000000	0.000000	0.000000
17	0	0.000000	0.000000	2.556770
17	0	0.000000	0.000000	-2.556770

MP2/S-TZPsp
Adduct **29**: $[Br\text{-}*\text{-}IBr]^-$
Symmetry $D_{\infty h}$
Energy MP2 = –12063.468574 au

53	0	0.000000	0.000000	0.000000
35	0	0.000000	0.000000	2.711416
35	0	0.000000	0.000000	-2.711416

MP2/S-TZPsp
Adduct **30**: $Me_2ClS\text{-}*\text{-}Cl$
Symmetry C_2
Energy MP2 = –1396.624999 au

16	0	0.000000	0.000000	0.291909
6	0	-1.388433	-0.000013	-0.863215
6	0	1.388433	0.000013	-0.863215
1	0	2.289353	0.000089	-0.254850
1	0	1.329633	0.905267	-1.457590

1	0	1.329720	-0.905300	-1.457508
1	0	-2.289353	-0.000089	-0.254850
1	0	-1.329633	-0.905267	-1.457590
1	0	-1.329720	0.905300	-1.457508
17	0	0.000000	2.268284	0.353763
17	0	0.000000	-2.268284	0.353763

MP2/S-TZPsp
Adduct **31**: Me_2BrS-*-Br
Symmetry C_{2v}
Energy MP2 = –5622.568576 au

16	0	0.000000	0.000000	0.143843
6	0	0.000000	1.383548	-1.021033
6	0	0.000000	-1.383548	-1.021033
1	0	0.000000	-2.288141	-0.418020
1	0	0.904992	-1.320394	-1.616137
1	0	-0.904992	-1.320394	-1.616137
1	0	0.000000	2.288141	-0.418020
1	0	-0.904992	1.320394	-1.616137
1	0	0.904992	1.320394	-1.616137
35	0	2.438973	0.000000	0.246450
35	0	-2.438973	0.000000	0.246450

MP2/S-TZPsp
Adduct **32**: Me_2ClSe-*-Cl
Symmetry C_2
Energy MP2 = –3399.019255 au

34	0	0.000000	0.000000	0.289711
6	0	0.000000	1.459584	-0.967379
6	0	0.000000	-1.459584	-0.967379
1	0	-0.233160	-2.356049	-0.399995
1	0	0.989977	-1.512002	-1.406516
1	0	-0.782969	-1.258989	-1.691067
1	0	0.233160	2.356049	-0.399995
1	0	-0.989977	1.512002	-1.406516
1	0	0.782969	1.258989	-1.691067
17	0	2.356040	0.065578	0.257456
17	0	-2.356040	-0.065578	0.257456

MP2/S-TZPsp
Adduct **33**: Me_2BrSe-*-Br
Symmetry C_2
Energy MP2 = –7624.961303 au

34	0	0.000000	0.000000	0.199985
6	0	0.000000	1.456095	-1.066366
6	0	0.000000	-1.456095	-1.066366
1	0	-0.236950	-2.354091	-0.502942
1	0	0.991443	-1.507512	-1.503065
1	0	-0.780175	-1.250685	-1.791857
1	0	0.236950	2.354091	-0.502942
1	0	-0.991443	1.507512	-1.503065
1	0	0.780175	1.250685	-1.791857
35	0	2.520383	0.077707	0.194181
35	0	-2.520383	-0.077707	0.194181

MP2/S-TZPsp
Adduct **34**: Me_2ClTe-*-Cl
Symmetry C_2
Energy MP2 = –7610.876421 au

52	0	0.000000	0.000000	0.323126
6	0	-1.612866	-0.054844	-1.021945
6	0	1.612866	0.054844	-1.021945
1	0	2.382776	0.682894	-0.583720
1	0	1.251416	0.514055	-1.938198
1	0	1.959106	-0.959889	-1.185187
1	0	-2.382776	-0.682894	-0.583720
1	0	-1.251416	-0.514055	-1.938198
1	0	-1.959106	0.959889	-1.185187
17	0	0.000000	2.453305	0.084559
17	0	0.000000	-2.453305	0.084559

MP2/S-TZPsp
Adduct **35**: Me_2BrTe-*-Br
Symmetry C_2
Energy MP2 = –11836.814172 au

52	0	0.000000	0.000000	0.299846
6	0	0.000000	1.605354	-1.061346
6	0	0.000000	-1.605354	-1.061346
1	0	-0.551977	-2.420905	-0.603478
1	0	1.029359	-1.875908	-1.270457
1	0	-0.526116	-1.268158	-1.950219
1	0	0.551977	2.420905	-0.603478
1	0	-1.029359	1.875908	-1.270457
1	0	0.526116	1.268158	-1.950219
35	0	2.616667	0.101196	0.068464
35	0	-2.616667	-0.101196	0.068464

MP2/S-TZPsp
Adduct **36**: Me_2ITe-*-I
Symmetry C_2
Energy MP2 = –20527.691134 au

52	0	0.000000	0.000000	0.285216
6	0	0.000000	1.605002	-1.086164
6	0	0.000000	-1.605002	-1.086164
1	0	-0.556396	-2.418353	-0.629445
1	0	1.028747	-1.878422	-1.295482
1	0	-0.524619	-1.262726	-1.973870
1	0	0.556396	2.418353	-0.629445
1	0	-1.028747	1.878422	-1.295482
1	0	0.524619	1.262726	-1.973870
53	0	2.860052	0.128890	0.056607
53	0	-2.860052	-0.128890	0.056607

MP2/S-TZPsp
Adduct **37**: Me_2S^+-*-Cl
Symmetry C_s
Energy MP2 = –936.684573 au

16	0	0.577251	0.311287	0.000000
6	0	-0.241085	1.088051	1.385730
1	0	0.102182	0.581109	2.284626
1	0	-1.318829	1.011762	1.264942

1	0	0.094361	2.125823	1.387843
6	0	-0.241085	1.088051	-1.385730
1	0	0.102182	0.581109	-2.284626
1	0	0.094361	2.125823	-1.387843
1	0	-1.318829	1.011762	-1.264942
17	0	-0.241085	-1.498505	0.000000

MP2/S-TZPsp
Adduct **38**: Me_2S^+-*-Br
Symmetry C_s
Energy MP2 = –3049.659036 au

16	0	0.655979	0.790644	0.000000
6	0	-0.182475	1.554219	1.386705
1	0	0.171136	1.057200	2.286860
1	0	-1.257972	1.451131	1.267067
1	0	0.127166	2.599711	1.386485
6	0	-0.182475	1.554219	-1.386705
1	0	0.171136	1.057200	-2.286860
1	0	0.127166	2.599711	-1.386485
1	0	-1.257972	1.451131	-1.267067
35	0	-0.182475	-1.186200	0.000000

MP2/S-TZPsp
Adduct **39**: Me_2S^+-*-I
Symmetry C_s
Energy MP2 = –7395.108976 au

16	0	1.349427	0.250104	0.000000
6	0	1.349427	1.392532	1.388533
1	0	1.229818	0.798568	2.291181
1	0	0.541621	2.110771	1.275067
1	0	2.325431	1.877377	1.381706
6	0	1.349427	1.392532	-1.388533
1	0	1.229818	0.798568	-2.291181
1	0	2.325431	1.877377	-1.381706
1	0	0.541621	2.110771	-1.275067
53	0	-0.867504	-0.571424	0.000000

MP2/S-TZPsp
Adduct **40**: Me_2Se^+-*-Cl
Symmetry C_s
Energy MP2 = –2939.067285 au

34	0	0.490088	0.240877	0.000000
6	0	-0.450748	1.054217	1.455379
1	0	-0.132471	0.550110	2.364040
1	0	-1.518216	0.946173	1.285268
1	0	-0.144967	2.100004	1.470751
6	0	-0.450748	1.054217	-1.455379
1	0	-0.132471	0.550110	-2.364040
1	0	-0.144967	2.100004	-1.470751
1	0	-1.518216	0.946173	-1.285268
17	0	-0.450748	-1.649000	0.000000

MP2/S-TZPsp
Adduct **41**: Me_2Se^+-*-Br
Symmetry C_s

Energy MP2 = –5052.042140 au

34	0	0.596231	0.650593	0.000000
6	0	-0.365313	1.447912	1.455863
1	0	-0.039333	0.949810	2.364926
1	0	-1.429950	1.316690	1.285103
1	0	-0.081781	2.499603	1.471641
6	0	-0.365313	1.447912	-1.455863
1	0	-0.039333	0.949810	-2.364926
1	0	-0.081781	2.499603	-1.471641
1	0	-1.429950	1.316690	-1.285103
35	0	-0.365313	-1.400780	0.000000

MP2/S-TZPsp
Adduct **42**: Me_2Se^+-*-I
Symmetry C_s
Energy MP2 = –9397.491362 au

34	0	0.672039	1.006432	0.000000
6	0	-0.308724	1.792946	1.457134
1	0	0.028246	1.306306	2.368200
1	0	-1.370640	1.637427	1.291036
1	0	-0.048730	2.850217	1.467361
6	0	-0.308724	1.792946	-1.457134
1	0	0.028246	1.306306	-2.368200
1	0	-0.048730	2.850217	-1.467361
1	0	-1.370640	1.637427	-1.291036
53	0	-0.308724	-1.270225	0.000000

MP2/S-TZPsp
Adduct **43**: Me_2Te^+-*-Cl
Symmetry C_s
Energy MP2 = –7150.912472 au

52	0	0.450517	0.197865	0.000000
6	0	-0.639917	1.077494	1.555198
1	0	-0.349957	0.601917	2.488616
1	0	-1.697578	0.930551	1.351341
1	0	-0.387111	2.136804	1.581274
6	0	-0.639917	1.077494	-1.555198
1	0	-0.349957	0.601917	-2.488616
1	0	-0.387111	2.136804	-1.581274
1	0	-1.697578	0.930551	-1.351341
17	0	-0.639917	-1.797498	0.000000

MP2/S-TZPsp
Adduct **44**: Me_2Te^+-*-Br
Symmetry C_s
Energy MP2 = –9263.885186 au

52	0	0.571185	0.561883	0.000000
6	0	-0.540643	1.422949	1.555731
1	0	-0.245113	0.948924	2.488099
1	0	-1.594634	1.256497	1.348740
1	0	-0.305965	2.486016	1.584558
6	0	-0.540643	1.422949	-1.555731
1	0	-0.245113	0.948924	-2.488099
1	0	-0.305965	2.486016	-1.584558
1	0	-1.594634	1.256497	-1.348740
35	0	-0.540643	-1.590748	0.000000

MP2/S-TZPsp
Adduct **45**: Me_2Te^+-*-I
Symmetry C_s
Energy MP2 = –13609.330466 au

52	0	0.663767	0.895711	0.000000
6	0	-0.471176	1.738710	1.557779
1	0	-0.169326	1.267171	2.489256
1	0	-1.521503	1.553348	1.349624
1	0	-0.253897	2.804982	1.587579
6	0	-0.471176	1.738710	-1.557779
1	0	-0.169326	1.267171	-2.489256
1	0	-0.253897	2.804982	-1.587579
1	0	-1.521503	1.553348	-1.349624
53	0	-0.471176	-1.484764	0.000000

MP2/S-TZPsp
Adduct **46**: Cl-*-Cl
Symmetry $D_{\infty h}$
Energy MP2 = –919.290787 au

17	0	0.000000	0.000000	0.995869
17	0	0.000000	0.000000	-0.995869

MP2/S-TZPsp
Adduct **47**: Br-*-Br
Symmetry $D_{\infty h}$
Energy MP2 = –5145.248000 au

35	0	0.000000	0.000000	1.137779
35	0	0.000000	0.000000	-1.137779

MP2/S-TZPsp
Adduct **48**: I-*-I
Symmetry $D_{\infty h}$
Energy MP2 = –13836.154371 au

53	0	0.000000	0.000000	1.327269
53	0	0.000000	0.000000	-1.327269

MP2/S-TZPsp
Adduct **49**: CH_3-*-Cl
Symmetry C_{3v}
Energy MP2 = –499.474395 au

6	0	0.000000	0.000000	-1.122759
17	0	0.000000	0.000000	0.655223
1	0	0.000000	1.027712	-1.467415
1	0	-0.890025	-0.513856	-1.467415
1	0	0.890025	-0.513856	-1.467415

MP2/S-TZPsp
Adduct **50**: CH_3-*-Br
Symmetry C_3
Energy MP2 = –2612.442905 au

6	0	0.000000	0.000000	-1.507569
35	0	0.000000	0.000000	0.416610

1	0	1.029151	0.000000	-1.845316
1	0	-0.514575	0.891271	-1.845316
1	0	-0.514575	-0.891271	-1.845316

MP2/S-TZPsp
Adduct **51**: CH_3-*-I
Symmetry C_{3v}
Energy MP2 = –6957.884713 au

6	0	0.000000	0.000000	-1.795480
53	0	0.000000	0.000000	0.324106
1	0	0.000000	1.028494	-2.134916
1	0	-0.890702	-0.514247	-2.134916
1	0	0.890702	-0.514247	-2.134916

MP2/S-TZPsp
Adduct **52**: CH_3-*-CH_3
Symmetry D_{3d}
Energy MP2 = –79.623437 au

6	0	0.000000	0.000000	0.761329
6	0	0.000000	0.000000	-0.761329
1	0	0.000000	1.014832	1.155955
1	0	-0.878870	-0.507416	1.155955
1	0	0.878870	-0.507416	1.155955
1	0	0.000000	-1.014832	-1.155955
1	0	-0.878870	0.507416	-1.155955
1	0	0.878870	0.507416	-1.155955

MP2/S-TZPsp
Adduct **53**: CH_2-*-CH_2
Symmetry D_{2h}
Energy MP2 = –78.393451 au

6	0	0.000000	0.000000	0.665891
6	0	0.000000	0.000000	-0.665891
1	0	0.000000	0.922897	1.228598
1	0	0.000000	-0.922897	1.228598
1	0	0.000000	0.922897	-1.228598
1	0	0.000000	-0.922897	-1.228598

MP2/S-TZPsp
Adduct **54**: CH-*-CH
Symmetry $D_{\infty h}$
Energy MP2 = –77.153193 au

6	0	0.000000	0.000000	0.606053
6	0	0.000000	0.000000	-0.606053
1	0	0.000000	0.000000	1.668691
1	0	0.000000	0.000000	-1.668691

MP2/S-TZPsp
Adduct **55**: CH_3-*-H
Symmetry T_d
Energy MP2 = –40.408730 au

6	0	0.000000	0.000000	0.000000
1	0	0.626906	0.626906	0.626906
1	0	-0.626906	-0.626906	0.626906

1	0	0.626906	-0.626906	-0.626906
1	0	-0.626906	0.626906	-0.626906

MP2/S-TZPsp
Adduct **56**: H-*-H
Symmetry $D_{\infty h}$
Energy MP2 = –1.164957 au

1	0	0.000000	0.000000	0.369143
1	0	0.000000	0.000000	-0.369143

MP2/S-TZPsp
Adduct **57a** (Type: **CC**)
Symmetry C_2
Energy MP2 = –1258.800858 au

6	0	0.000000	0.000000	0.575113
6	0	0.000000	0.000000	2.018700
6	0	0.000000	1.282143	-0.072651
6	0	-0.066547	1.209787	2.744593
6	0	0.000000	-1.282143	-0.072651
6	0	0.066547	-1.209787	2.744593
6	0	-0.095041	2.439804	0.689618
6	0	-0.134058	2.412357	2.089726
6	0	0.095041	-2.439804	0.689618
6	0	0.134058	-2.412357	2.089726
1	0	-0.065811	1.162016	3.826509
1	0	0.065811	-1.162016	3.826509
1	0	-0.134038	3.399146	0.196514
1	0	-0.203096	3.341017	2.641002
1	0	0.134038	-3.399146	0.196514
1	0	0.203096	-3.341017	2.641002
16	0	0.201178	1.439604	-1.826344
6	0	0.861576	3.113006	-1.971976
1	0	0.099146	3.874793	-1.826393
1	0	1.687082	3.263000	-1.278628
1	0	1.228660	3.179245	-2.994789
16	0	-0.201178	-1.439604	-1.826344
6	0	-0.861576	-3.113006	-1.971976
1	0	-0.099146	-3.874793	-1.826393
1	0	-1.687082	-3.263000	-1.278628
1	0	-1.228660	-3.179245	-2.994789

MP2/S-TZPsp
Adduct **57a** (Type: **AB**)
Symmetry C_1
Energy MP2 = –1258.803352 au

6	0	0.500900	0.331404	-0.088920
6	0	1.467183	1.396081	0.036323
6	0	1.027809	-0.986268	-0.269342
6	0	2.845018	1.140744	-0.146070
6	0	-0.890804	0.691574	-0.023961
6	0	1.060155	2.715231	0.332998
6	0	2.389216	-1.186436	-0.448184
6	0	3.303319	-0.124460	-0.418783
6	0	-1.232258	2.000992	0.296436
6	0	-0.270559	3.002783	0.492630
1	0	3.533118	1.973603	-0.064543

1	0	2.737733	-2.202172	-0.581853
1	0	4.358386	-0.311212	-0.568748
1	0	-2.269863	2.280993	0.380455
1	0	-0.593729	4.005604	0.740085
1	0	1.816495	3.483882	0.431752
16	0	0.049977	-2.463314	-0.199934
6	0	-0.322941	-2.457107	1.571185
1	0	0.596902	-2.504006	2.150371
1	0	-0.900801	-1.573139	1.834074
1	0	-0.923137	-3.344816	1.765233
16	0	-2.170810	-0.461854	-0.443160
6	0	-3.637026	0.590071	-0.419502
1	0	-3.868804	0.957711	0.578456
1	0	-3.552509	1.418120	-1.121182
1	0	-4.440532	-0.069535	-0.743463

MP2/S-TZPsp
Adduct **57b** (Type: **AA**)
Symmetry C_1
Energy MP2 = –1333.898245 au

6	0	-0.698741	0.258366	0.006046
6	0	-1.822278	1.160241	-0.022734
6	0	-0.983094	-1.129319	0.181126
6	0	-3.127854	0.676065	0.219055
6	0	0.594643	0.840033	-0.147009
6	0	-1.628313	2.536129	-0.282945
6	0	-2.278560	-1.559473	0.420455
6	0	-3.352926	-0.657290	0.463901
6	0	0.744871	2.185780	-0.414834
6	0	-0.368411	3.038029	-0.498829
1	0	-2.450853	-2.620204	0.548566
1	0	-4.353855	-1.019432	0.657584
1	0	-3.948999	1.382612	0.208360
1	0	1.754474	2.562421	-0.532728
1	0	-0.225033	4.089407	-0.710667
1	0	-2.496444	3.183591	-0.309155
6	0	0.544813	-2.303960	-1.739463
1	0	1.323348	-3.031438	-1.962705
1	0	-0.365938	-2.563691	-2.273829
1	0	0.890434	-1.313834	-2.031103
6	0	2.074806	-0.125334	1.836931
1	0	2.950337	-0.671385	2.183252
1	0	2.093657	0.899789	2.204621
1	0	1.161502	-0.637494	2.126336
8	0	3.245145	1.051231	-0.193429
16	0	0.262320	-2.381775	0.045659
16	0	2.207210	-0.004837	0.036134

MP2/S-TZPsp
Adduct **57c** (Type: **AA**)
Symmetry C_2
Energy MP2 = –1408.986459 au

6	0	0.000000	0.000000	0.825270
6	0	0.000000	0.000000	2.265755
6	0	0.000000	1.274225	0.189283
6	0	-0.078757	1.219826	2.976671
6	0	0.000000	-1.274225	0.189283

6	0	0.078757	-1.219826	2.976671
6	0	-0.093821	2.446056	0.910070
6	0	-0.145596	2.421352	2.313433
6	0	0.093821	-2.446056	0.910070
6	0	0.145596	-2.421352	2.313433
1	0	-0.111050	3.377965	0.356691
1	0	-0.220315	3.348892	2.865353
1	0	-0.091025	1.184089	4.059250
1	0	0.111050	-3.377965	0.356691
1	0	0.220315	-3.348892	2.865353
1	0	0.091025	-1.184089	4.059250
6	0	1.935489	1.219705	-1.625732
1	0	2.256188	1.284740	-2.663659
1	0	2.397574	2.004141	-1.027984
1	0	2.150119	0.233754	-1.219297
6	0	-1.935489	-1.219705	-1.625732
1	0	-2.256188	-1.284740	-2.663659
1	0	-2.397574	-2.004141	-1.027984
1	0	-2.150119	-0.233754	-1.219297
8	0	-0.008362	-3.008643	-1.829506
8	0	0.008362	3.008643	-1.829506
16	0	0.158626	1.539323	-1.599359
16	0	-0.158626	-1.539323	-1.599359

MP2/S-TZPsp
Adduct **58a** (Type: **AB**)
Symmetry C_1
Energy MP2 = –3261.178950 au

6	0	-3.588397	-0.420629	-0.517946
6	0	-3.273847	0.885621	-0.232961
6	0	-1.939298	1.279566	0.014217
6	0	-0.867873	0.315834	-0.057648
6	0	-1.251136	-1.046596	-0.252879
6	0	-2.572958	-1.387404	-0.496137
1	0	-2.502999	3.325743	0.379297
1	0	-4.611122	-0.712000	-0.717182
1	0	-4.046328	1.644200	-0.191149
6	0	-1.673884	2.631385	0.322272
6	0	0.474310	0.803375	0.074091
1	0	-2.811300	-2.433311	-0.639079
6	0	0.676368	2.137180	0.404244
6	0	-0.385166	3.043447	0.547340
1	0	1.678097	2.513045	0.539941
1	0	-0.172155	4.072469	0.806617
16	0	-0.115007	-2.396648	-0.107003
34	0	2.009170	-0.270171	-0.322653
6	0	3.361229	1.121742	-0.281683
1	0	3.131278	1.918369	-0.985106
1	0	3.512342	1.518081	0.719249
1	0	4.269333	0.612193	-0.599825
6	0	0.126020	-2.344288	1.687096
1	0	0.514681	-1.372273	1.984607
1	0	-0.808894	-2.560309	2.199734
1	0	0.863206	-3.109422	1.925123

MP2/S-TZPsp
Adduct **58b** (Type: **AA**)

Symmetry C_1
Energy MP2 = –3336.261755 au

6	0	3.671286	-0.654601	0.480228
6	0	3.450995	0.680633	0.238434
6	0	2.148828	1.168872	-0.014123
6	0	1.026619	0.266029	-0.004534
6	0	1.306180	-1.119488	0.180207
6	0	2.596007	-1.556532	0.431194
1	0	2.814004	3.198836	-0.274821
1	0	4.670216	-1.018053	0.681643
1	0	4.274232	1.384931	0.240234
6	0	1.949619	2.545790	-0.264089
6	0	-0.263553	0.838182	-0.179785
1	0	2.764650	-2.616787	0.568065
6	0	-0.422600	2.184971	-0.427928
6	0	0.688326	3.043906	-0.485825
1	0	-1.437335	2.554099	-0.547261
1	0	0.542824	4.097698	-0.684386
16	0	0.038225	-2.347770	0.044295
6	0	-1.847697	-0.152391	1.921228
1	0	-0.923730	-0.646317	2.207783
1	0	-1.873450	0.884965	2.248301
1	0	-2.713734	-0.693850	2.294565
6	0	-0.185633	-2.311575	-1.751898
1	0	-0.422262	-1.302165	-2.085041
1	0	0.712199	-2.671794	-2.248090
1	0	-1.023809	-2.968217	-1.978247
34	0	-2.007931	-0.055473	-0.009779
8	0	-3.054501	1.205536	-0.192202

MP2/S-TZPsp
Adduct **58b**' (Type: **AA**)
Symmetry C_1
Energy MP2 = –3336.270706 au

6	0	-2.491988	2.290403	0.532456
6	0	-3.128105	1.094125	0.311186
6	0	-2.387499	-0.077360	0.032816
6	0	-0.945794	-0.040922	-0.006446
6	0	-0.338633	1.241689	0.146945
6	0	-1.093236	2.361987	0.431336
1	0	-4.159472	-1.273220	-0.197623
1	0	-3.061167	3.182488	0.758284
1	0	-4.208599	1.024090	0.346317
6	0	-3.076362	-1.285611	-0.216141
6	0	-0.272828	-1.285169	-0.191303
1	0	-0.567038	3.302760	0.545769
6	0	-0.988984	-2.446424	-0.434276
6	0	-2.391914	-2.448114	-0.475401
1	0	-0.443195	-3.371646	-0.564344
1	0	-2.924902	-3.368509	-0.673844
6	0	1.721617	-1.115283	1.863293
1	0	1.404381	-0.093858	2.059348
1	0	1.109780	-1.826100	2.410960
1	0	2.766439	-1.229696	2.144206
6	0	1.377515	1.461058	-1.865424
1	0	0.985017	0.485448	-2.138232
1	0	0.738287	2.264936	-2.228293
1	0	2.395125	1.584634	-2.231124

34	0	1.615290	-1.493273	-0.033022
16	0	1.431121	1.656254	-0.066847
8	0	1.530602	3.135948	0.148326

MP2/S-TZPsp
Adduct **58c** (Type: **AA**)
Symmetry C_1
Energy MP2 = –3411.347479 au

6	0	3.624074	0.377873	0.431436
6	0	3.101512	1.634274	0.236308
6	0	1.718176	1.822572	0.009271
6	0	0.829681	0.689086	-0.012245
6	0	1.434222	-0.590146	0.126743
6	0	2.782653	-0.745265	0.365318
1	0	1.900833	3.957777	-0.180204
1	0	4.681464	0.247931	0.619884
1	0	3.741653	2.507869	0.260874
6	0	1.207409	3.125540	-0.189970
6	0	-0.557629	0.962422	-0.166640
1	0	3.164362	-1.752388	0.486796
6	0	-1.023415	2.243790	-0.366495
6	0	-0.135966	3.333177	-0.392594
1	0	-2.095414	2.376868	-0.478796
1	0	-0.517323	4.332944	-0.553278
6	0	-1.877173	-0.422353	1.891993
1	0	-0.868303	-0.707537	2.179464
1	0	-2.129634	0.575783	2.243356
1	0	-2.603284	-1.151818	2.242483
6	0	0.460475	-2.090056	-1.828574
1	0	0.003111	-1.160305	-2.162600
1	0	1.489954	-2.168041	-2.175284
1	0	-0.125786	-2.946640	-2.155492
34	0	-2.033310	-0.324136	-0.036825
8	0	-3.358670	0.627561	-0.242901
16	0	0.519776	-2.137779	-0.025797
8	0	1.457467	-3.244166	0.331686

MP2/S-TZPsp
Adduct **59a** (Type: **CC**)
Symmetry C_2
Energy MP2 = –5263.548709 au

6	0	0.000000	0.000000	1.039501
6	0	0.000000	0.000000	2.481966
6	0	0.000000	1.269841	0.387925
6	0	-0.096902	1.213918	3.197815
6	0	0.000000	-1.269841	0.387925
6	0	0.096902	-1.213918	3.197815
6	0	-0.133290	2.432140	1.131298
6	0	-0.190438	2.411640	2.532906
6	0	0.133290	-2.432140	1.131298
6	0	0.190438	-2.411640	2.532906
1	0	-0.100874	1.176422	4.280411
1	0	0.100874	-1.176422	4.280411
1	0	-0.175532	3.384422	0.620362
1	0	-0.288552	3.340219	3.079951
1	0	0.175532	-3.384422	0.620362
1	0	0.288552	-3.340219	3.079951

34	0	0.358666	1.477615	-1.479297
6	0	1.597831	2.967039	-1.308254
1	0	1.080536	3.904722	-1.130113
1	0	2.304295	2.758544	-0.509431
1	0	2.123398	3.022863	-2.259625
34	0	-0.358666	-1.477615	-1.479297
6	0	-1.597831	-2.967039	-1.308254
1	0	-1.080536	-3.904722	-1.130113
1	0	-2.304295	-2.758544	-0.509431
1	0	-2.123398	-3.022863	-2.259625

MP2/S-TZPsp
Adduct **59a** (Type: **AB**)
Symmetry C_1
Energy MP2 = –5263.550729 au

6	0	0.841357	0.646446	-0.056679
6	0	1.871771	1.655859	0.012480
6	0	1.282569	-0.694631	-0.265437
6	0	3.216741	1.326014	-0.267700
6	0	-0.517218	1.080707	0.094160
6	0	1.556058	2.989011	0.353231
6	0	2.613197	-0.973460	-0.536486
6	0	3.582825	0.038892	-0.576213
6	0	-0.768718	2.396264	0.461120
6	0	0.256478	3.342052	0.612543
1	0	3.955404	2.117745	-0.229266
1	0	2.902586	-2.005842	-0.682120
1	0	4.612967	-0.204701	-0.800061
1	0	-1.783390	2.726248	0.619027
1	0	0.006033	4.354565	0.901559
1	0	2.356981	3.715851	0.409224
34	0	0.160520	-2.219429	-0.053431
6	0	-0.107839	-2.003610	1.854932
1	0	0.846172	-2.066953	2.370715
1	0	-0.597048	-1.051681	2.045544
1	0	-0.758585	-2.815718	2.172563
34	0	-2.017604	-0.026799	-0.344263
6	0	-3.392152	1.345517	-0.370605
1	0	-3.613797	1.726447	0.622979
1	0	-3.126885	2.154091	-1.047453
1	0	-4.270013	0.827321	-0.753184

MP2/S-TZPsp
Adduct **59b** (Type: **AA**)
Symmetry C_1
Energy MP2 = –5338.634131 au

6	0	-1.047283	0.524594	-0.005181
6	0	-2.183135	1.413175	-0.021469
6	0	-1.314126	-0.861388	0.189303
6	0	-3.478599	0.913589	0.241544
6	0	0.233079	1.120182	-0.185385
6	0	-2.007812	2.789927	-0.289129
6	0	-2.598345	-1.310560	0.446650
6	0	-3.683651	-0.420959	0.496890
6	0	0.367742	2.466697	-0.449709
6	0	-0.756361	3.306668	-0.520261
1	0	-2.760065	-2.371489	0.585007

1	0	-4.677549	-0.794360	0.705037
1	0	-4.308997	1.609444	0.238464
1	0	1.376271	2.852961	-0.568186
1	0	-0.628294	4.359987	-0.732729
1	0	-2.883736	3.427335	-0.305515
6	0	0.294823	-2.003723	-1.881344
1	0	1.133582	-2.641183	-2.152171
1	0	-0.602757	-2.321995	-2.402980
1	0	0.532555	-0.969474	-2.120177
34	0	2.004539	0.279187	0.010975
6	0	1.811239	0.182016	1.939915
1	0	2.655427	-0.381411	2.330181
1	0	1.856185	1.219583	2.264514
1	0	0.869042	-0.286317	2.209467
8	0	3.014793	1.571777	-0.156739
34	0	0.039419	-2.190911	0.031144

MP2/S-TZPsp
Adduct **59c** (Type: **AA**)
Symmetry C_2
Energy MP2 = –5413.707013 au

6	0	0.000000	0.000000	1.225147
6	0	0.000000	0.000000	2.666345
6	0	0.000000	1.271049	0.590171
6	0	-0.068110	1.222316	3.373908
6	0	0.000000	-1.271049	0.590171
6	0	0.068110	-1.222316	3.373908
6	0	-0.076421	2.446437	1.304011
6	0	-0.123928	2.423695	2.708458
6	0	0.076421	-2.446437	1.304011
6	0	0.123928	-2.423695	2.708458
1	0	-0.077013	3.377608	0.745680
1	0	-0.185956	3.352619	3.259760
1	0	-0.078273	1.189657	4.456723
1	0	0.077013	-3.377608	0.745680
1	0	0.185956	-3.352619	3.259760
1	0	0.078273	-1.189657	4.456723
6	0	2.095419	1.190159	-1.268367
1	0	2.474325	1.226502	-2.286720
1	0	2.528496	1.982819	-0.662038
1	0	2.261780	0.211682	-0.823100
34	0	-0.199689	-1.585972	-1.325912
6	0	-2.095419	-1.190159	-1.268367
1	0	-2.474325	-1.226502	-2.286720
1	0	-2.528496	-1.982819	-0.662038
1	0	-2.261780	-0.211682	-0.823100
8	0	-0.161728	-3.225143	-1.441607
34	0	0.199689	1.585972	-1.325912
8	0	0.161728	3.225143	-1.441607

Appendix

QTAIM Dual Functional Analysis (QTAIM-DFA)

The bond critical point (BCP; ∗) is an important concept in QTAIM. The BCP of $(\omega, \sigma) = (3, -1)$[SA1] is a point along the bond path (BP) at the interatomic surface, where charge density $\rho(\boldsymbol{r})$ reaches a minimum. It is donated by $\rho_b(\boldsymbol{r}_c)$, so are other QTAIM functions, such as the total electron energy densities $H_b(\boldsymbol{r}_c)$, potential energy densities $V_b(\boldsymbol{r}_c)$ and kinetic energy densities $G_b(\boldsymbol{r}_c)$ at the BCPs. A chemical bond or interaction between A and B is denoted by A–B, which corresponds to the BP between A and B in QTAIM. We will use A-∗-B for BP, where the asterisk emphasizes the presence of a BCP in A–B.

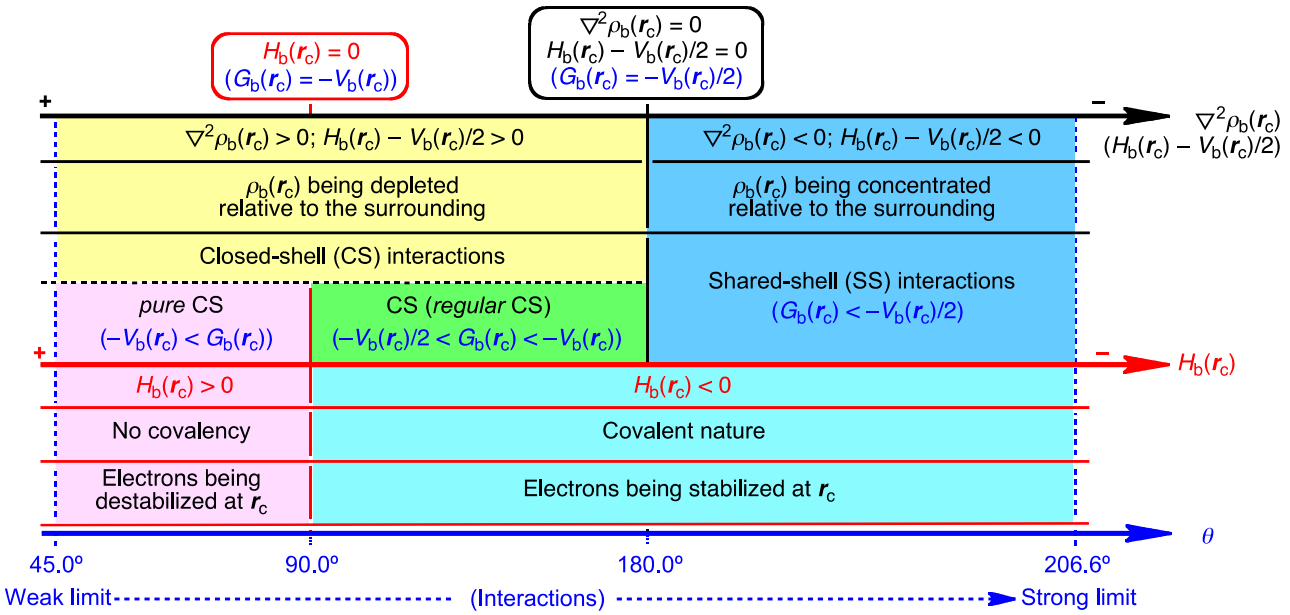
The sign of the Laplacian $\rho_b(\boldsymbol{r}_c)$ ($\nabla^2\rho_b(\boldsymbol{r}_c)$) indicates that $\rho_b(\boldsymbol{r}_c)$ is depleted or concentrated with respect to its surrounding, since $\nabla^2\rho_b(\boldsymbol{r}_c)$ is the second derivative of $\rho_b(\boldsymbol{r}_c)$. $\rho_b(\boldsymbol{r}_c)$ is locally depleted relative to the average distribution around $\boldsymbol{r}_c$ if $\nabla^2\rho_b(\boldsymbol{r}_c) > 0$, but it is concentrated when $\nabla^2\rho_b(\boldsymbol{r}_c) < 0$. Total electron energy densities at BCPs ($H_b(\boldsymbol{r}_c)$) must be a more appropriate measure for weak interactions on the energy basis.[SA1–SA8] $H_b(\boldsymbol{r}_c)$ are the sum of kinetic energy densities ($G_b(\boldsymbol{r}_c)$) and potential energy densities ($V_b(\boldsymbol{r}_c)$) at BCPs, as shown in eq (SA1). Electrons at BCPs are stabilized when $H_b(\boldsymbol{r}_c) < 0$, therefore, interactions exhibit the covalent nature in this region, whereas they exhibit no covalency if $H_b(\boldsymbol{r}_c) > 0$, due to the destabilization of electrons at BCPs under the conditions.[SA1] Eqs (SA2) and (SA2') represent the relations between $\nabla^2\rho_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c)$, together with $G_b(\boldsymbol{r}_c)$ and $V_b(\boldsymbol{r}_c)$, which are closely related to the virial theorem.

$$H_b(\boldsymbol{r}_c) = G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c) \quad \text{(SA1)}$$

$$(\hbar^2/8m)\nabla^2\rho_b(\boldsymbol{r}_c) = H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 \quad \text{(SA2)}$$

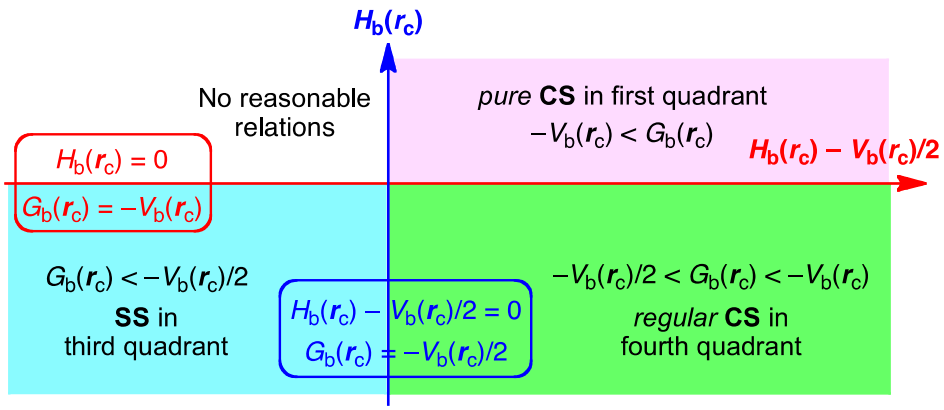
$$= G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c)/2 \quad \text{(SA2')}$$

Interactions are classified by the signs of $\nabla^2\rho_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c)$. Interactions in the region of $\nabla^2\rho_b(\boldsymbol{r}_c) < 0$ are called shared-shell (SS) interactions and they are closed-shell (CS) interactions for $\nabla^2\rho_b(\boldsymbol{r}_c) > 0$. $H_b(\boldsymbol{r}_c)$ must be negative when $\nabla^2\rho_b(\boldsymbol{r}_c) < 0$, since $H_b(\boldsymbol{r}_c)$ are larger than $(\hbar^2/8m)\nabla^2\rho_b(\boldsymbol{r}_c)$ by $V_b(\boldsymbol{r}_c)/2$ with negative $V_b(\boldsymbol{r}_c)$ at all BCPs (eq (SA2)). Consequently, $\nabla^2\rho_b(\boldsymbol{r}_c) < 0$ and $H_b(\boldsymbol{r}_c) < 0$ for the SS interactions. The CS interactions are especially called *pure* CS interactions for $H_b(\boldsymbol{r}_c) > 0$ and $\nabla^2\rho_b(\boldsymbol{r}_c) > 0$, since electrons at BCPs are depleted and destabilized under the conditions.[SA1a] Electrons in the intermediate region between SS and *pure* CS, which belong to CS, are locally depleted but stabilized at BCPs, since $\nabla^2\rho_b(\boldsymbol{r}_c) > 0$ but $H_b(\boldsymbol{r}_c) < 0$.[SA1a] We call the interactions in this region *regular* CS,[SA4,SA5] when it is necessary to distinguish from *pure* CS. The role of $\nabla^2\rho_b(\boldsymbol{r}_c)$ in the classification can be replaced by $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$, since $(\hbar^2/8m)\nabla^2\rho_b(\boldsymbol{r}_c) = H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ (eq (SA2)). Scheme SA1 summarizes the classification.



Scheme SA1. Classification of interactions by the signs of $\nabla^2\rho_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c)$, together with $G_b(\boldsymbol{r}_c)$ and $V_b(\boldsymbol{r}_c)$.

We proposed QTAIM-DFA by plotting $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ (= $(\hbar^2/8m)\nabla^2\rho_b(\boldsymbol{r}_c)$),[SA4a] after the proposal of $H_b(\boldsymbol{r}_c)$ versus $\nabla^2\rho_b(\boldsymbol{r}_c)$.[SA4b] Both axes in the plot of the former are given in energy unit, therefore, distances on the (x, y) (= $(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2, H_b(\boldsymbol{r}_c))$ plane can be expressed in the energy unit, which provides an analytical development. QTAIM-DFA incorporates the classification of interactions by the signs of $\nabla^2\rho_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c)$. Scheme S2 summarizes the QTAIM-DFA treatment. Interactions of *pure* CS appear in the first quadrant, those of *regular* CS in the fourth quadrant and SS interactions do in the third quadrant. No interactions appear in the second one.



Scheme SA2. QTAIM-DFA: Plot of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ for Weak to Strong Interactions.

In our treatment, data for perturbed structures around fully optimized structures are also employed for the plots, together with the fully optimized ones (see Fig. SA1).[SA4–SA8] We proposed the concept of the "dynamic nature of interaction" originated from the perturbed structures. The behavior of interactions at the fully optimized structures corresponds to "the static nature of interactions", whereas that containing

perturbed structures exhibit the "dynamic nature of interaction" as explained below. The method to generate the perturbed structures is discussed later. Plots of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ are analyzed employing the polar coordinate (R, θ) representation with (θ_p, κ_p) parameters.[SA4a,SA5–SA8] Fig. SA1 explains the treatment. R in (R, θ) is defined by eq (SA3) and given in the energy unit. Indeed, R does not correspond to the usual interaction energy, but it does to the local energy at BCP, expressed by $[(H_b(\boldsymbol{r}_c))^2 + (H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)^2]^{1/2}$ in the plot (cf: eq (SA3)), where $R = 0$ for the enough large interaction distance. The plots show a spiral stream, as a whole. θ in (R, θ) defined by eq (SA4), measured from the y-axis, controls the spiral stream of the plot. Each plot for an interaction shows a specific curve, which provides important information of the interaction (see Fig. SA1). The curve is expressed by θ_p and κ_p. While θ_p, defined by eq (SA5) and measured from the y-direction, corresponds to the tangent line of a plot, where θ_p is calculated employing data of the perturbed structures with a fully-optimized structure and κ_p is the curvature of the plot (eq (SA6)). While (R, θ) correspond to the static nature, (θ_p, κ_p) represent the dynamic nature of interactions. We call (R, θ) and (θ_p, κ_p) QTAIM-DFA parameters, whereas $\rho_b(\boldsymbol{r}_c)$, $\nabla^2\rho_b(\boldsymbol{r}_c)$, $G_b(\boldsymbol{r}_c)$, $V_b(\boldsymbol{r}_c)$, $H_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ belong to QTAIM functions. $k_b(\boldsymbol{r}_c)$, defined by eq (SA7), is an QTAIM function but it will be treated as if it were an QTAIM-DFA parameter, if suitable.

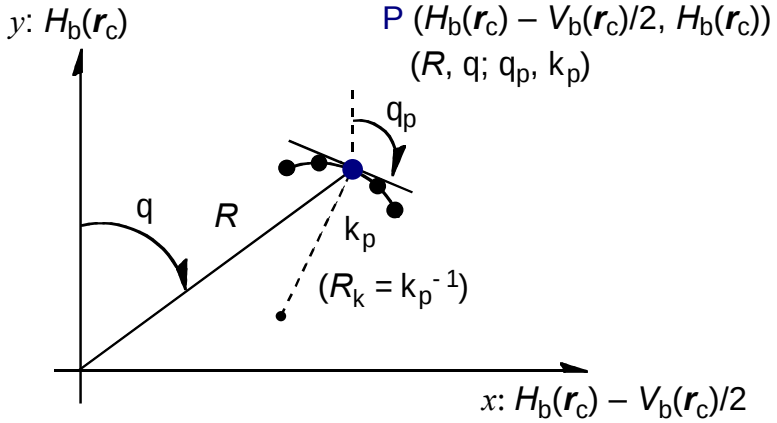


Figure SA1. Polar (R, θ) coordinate representation of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$, with ($\theta_p$, κ_p) parameters.

$$R = (x^2 + y^2)^{1/2} \quad \text{(SA3)}$$

$$\theta = 90^o - \tan^{-1}(y/x) \quad \text{(SA4)}$$

$$\theta_p = 90^o - \tan^{-1}(dy/dx) \quad \text{(SA5)}$$

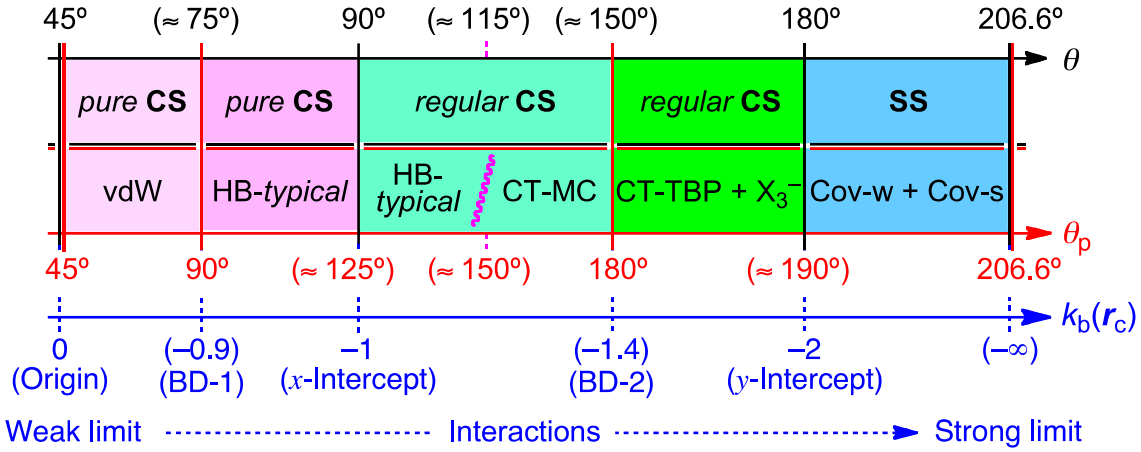
$$\kappa_p = |d^2y/dx^2| / [1 + (dy/dx)^2]^{3/2} \quad \text{(SA6)}$$

$$k_b(\boldsymbol{r}_c) = V_b(\boldsymbol{r}_c)/G_b(\boldsymbol{r}_c) \quad \text{(SA7)}$$

where $(x, y) = (H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2, H_b(\boldsymbol{r}_c))$

Criteria for Classification of Interactions: Behavior of Typical Interactions Elucidated by QTAIM-DFA

$H_b(\boldsymbol{r}_c)$ are plotted versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ for typical interactions in vdW (van der Waals interactions), HBs (hydrogen bonds), CT-MCs (molecular complexes through charge transfer), X_3^- (trihalide ions), CT-TBPs (trigonal bipyramidal adducts through charge-transfer), Cov-w (weak covalent bonds) and Cov-s (strong covalent bonds).[SA4–SA8] Rough criteria are obtained by applying QTAIM-DFA, after the analysis of the plots for the typical interactions according to eqs (SA3)–(SA7). Scheme SA3 shows the rough criteria, which are accomplished by the θ and θ_p values, together with the values of $k_b(\boldsymbol{r}_c)$. The criteria will be employed to discuss the nature of interactions in question, as a reference.



Scheme SA3. Rough classification and characterization of interactions by θ and θ_p, together with $k_b(\boldsymbol{r}_c)$ (= $V_b(\boldsymbol{r}_c)/G_b(\boldsymbol{r}_c)$).

Characterization of interactions

The characterization of interactions is explained employing $[^1Cl\text{-}^2Cl\text{-}^3Cl]^-$. The wide range of the perturbed structures were generated by partially optimizing $r(^2Cl\text{-}^3Cl)$ in $[^1Cl\text{-}^2Cl\text{-}^3Cl]^-$, assuming the $C_{\infty v}$ symmetry, with $r(^1Cl\text{-}^2Cl)$ being fixed in the wide range. The partial optimization method is called POM.[SA4b,SA5] The QTAIM functions, such as $V_b(\boldsymbol{r}_c)$, $G_b(\boldsymbol{r}_c)$, $H_b(\boldsymbol{r}_c)$, $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ are calculated at BCPs for the wide varieties of the perturbed structures of $[^1Cl\text{-}^2Cl\text{-}^3Cl]^-$. $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ and $H_b(\boldsymbol{r}_c)$ are plotted versus the interaction distances $r(^1Cl\text{-}^2Cl)$ in the perturbed structures of $[^1Cl\text{-}^2Cl\text{-}^3Cl]^-$, in the wide range. Figure SA2 shows the plots. Each plot is analyzed using a regression curve of the ninth function and the first derivative of each regression curve is obtained. As shown in Figure SA2, the maximum value of $H_b(\boldsymbol{r}_c)$ ($d(H_b(\boldsymbol{r}_c))/dr = 0$) is defined as the borderline between vdW and t-HB interactions. Similarly, the maximum value of $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ ($d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)/dr = 0$) does to the borderline between CT-MC and CT-TBP. However, it seems difficult to find a characteristic point corresponding to the borderline between *t*-HB and CT-MC in nature. Therefore, the borderline is tentatively given by $\theta_p = 150°$ based on the expectation form the experimental results, where θ_p is defined by $[90° - \tan^{-1}[dH_b(\boldsymbol{r}_c)/d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)]]$ in the plot of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$. The proposed classification and characterization of interactions, by means of the QTAIM functions of $H_b(\boldsymbol{r}_c)$, $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$, $G_b(\boldsymbol{r}_c)$ and/or $V_b(\boldsymbol{r}_c)$, are summarized in Table SA1. The plot of $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ versus w in Fig. SA2 is essentially the same as that of $\nabla^2\rho_b(\boldsymbol{r}_c)$ versus d(H---F) in X–H---F–Y, presented by Espinosa and co-workers.[SA9]

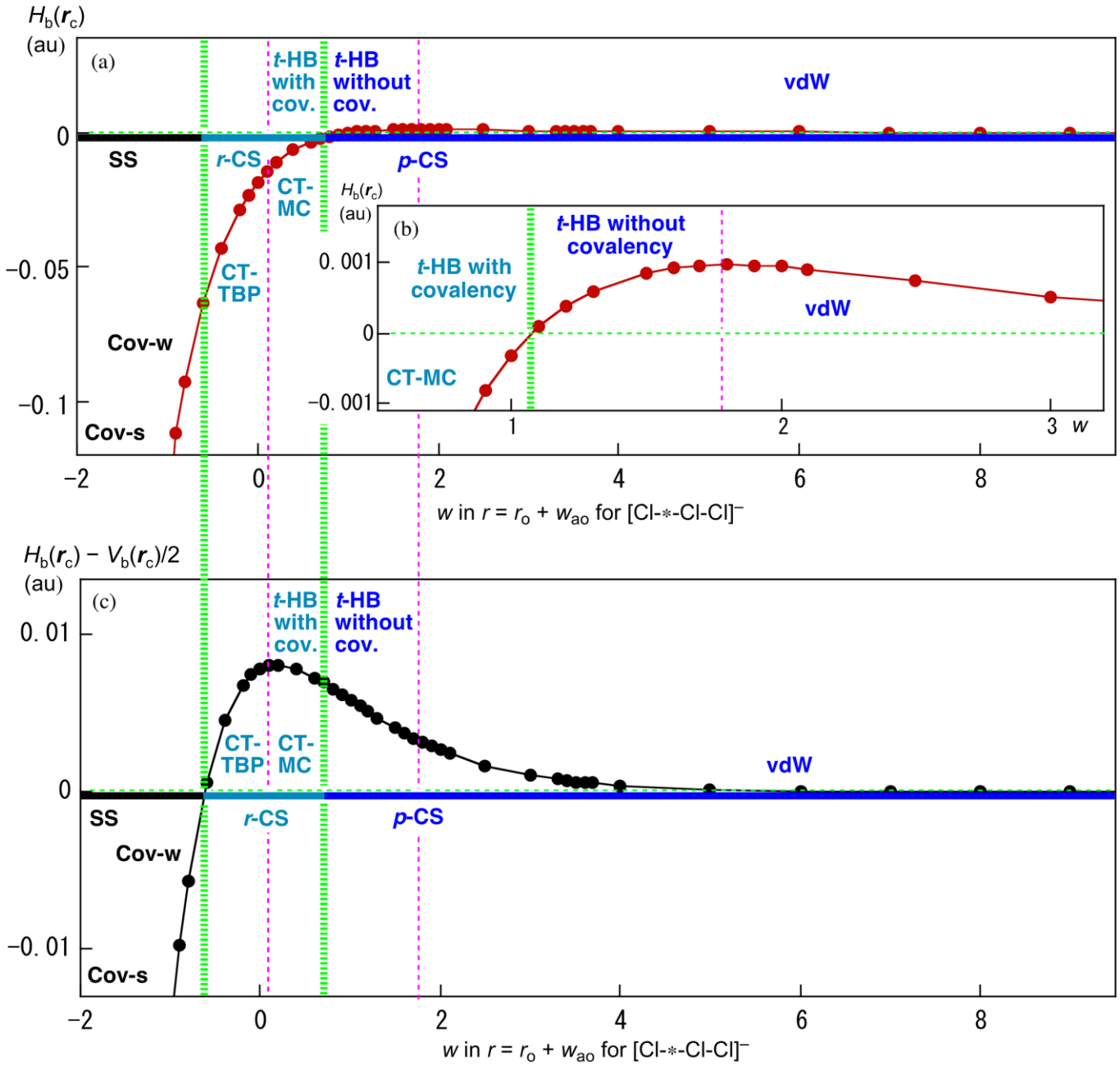


Figure SA2 Plot of $H_b(\boldsymbol{r}_c)$ versus w in $r(^1\text{Cl-}^2\text{Cl}) = r_o(^1\text{Cl-}^2\text{Cl}) + wa_o$ for $^1\text{Cl-}^2\text{Cl-}^3\text{Cl}^-$ (a) with the magnified picture of (a) (b) and that of $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ versus w (c). Typical hydrogen bonds without covalency and typical hydrogen bonds with covalency are abbreviated as *t*-HB without cov. and *t*-HB with cov., respectively, whereas Cov-w and Cov-s stand for weak covalent bonds and strong covalent bonds, respectively.

Table SA1. Proposed definitions for the classification and characterization of interactions by the signs $H_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ and their first derivatives, together with the tentatively proposed definitions by the characteristic points on the plots of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$. The tentatively proposed definitions are shown by italic. The requirements for the interactions are also shown.

ChP/Interaction	Requirements by $H_b(\boldsymbol{r}_c)$ and $V_b(\boldsymbol{r}_c)$	Requirements by $G_b(\boldsymbol{r}_c)$ and $V_b(\boldsymbol{r}_c)$
Origin	$H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 = 0$; $H_b(\boldsymbol{r}_c) = 0$	$G_b(\boldsymbol{r}_c) = 0$; $V_b(\boldsymbol{r}_c) = 0$
vdW	$H_b(\boldsymbol{r}_c) > 0$; $dH_b(\boldsymbol{r}_c)/d(-r) > 0$	$G_b(\boldsymbol{r}_c) > -V_b(\boldsymbol{r}_c)$; $dG_b(\boldsymbol{r}_c)/d(-r) > -dV_b(\boldsymbol{r}_c)/d(-r)$
Borderline (BD-1)	$H_b(\boldsymbol{r}_c) > 0$; $dH_b(\boldsymbol{r}_c)/d(-r) = 0$	$G_b(\boldsymbol{r}_c) > -V_b(\boldsymbol{r}_c)$; $dG_b(\boldsymbol{r}_c)/d(-r) = -dV_b(\boldsymbol{r}_c)/d(-r)$
t-HB$_{\text{with no covalency}}$	$H_b(\boldsymbol{r}_c) > 0$; $dH_b(\boldsymbol{r}_c)/d(-r) < 0$	$G_b(\boldsymbol{r}_c) > -V_b(\boldsymbol{r}_c)$; $dG_b(\boldsymbol{r}_c) < -dV_b(\boldsymbol{r}_c)$
Borderline (*x*-intercept)	$H_b(\boldsymbol{r}_c) = 0$ ($\theta_p{}^a = 125^o$)	$G_b(\boldsymbol{r}_c) = -V_b(\boldsymbol{r}_c)$ ($\theta_p{}^a = 125^o$)
t-HB$_{\text{with covalency}}$	$H_b(\boldsymbol{r}_c) < 0$; ($125^o <$) $\theta_p{}^a < 150^o$	$G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)$; ($125^o <$) $\theta_p{}^b < 150^o$
Borderline (Tentative)	$\theta_p{}^a = 150^o$	$\theta_p{}^b = 150^o$
CT-MC	$d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)/d(-r) > 0$; $150^o < \theta_p{}^a < 180^o$	$dG_b(\boldsymbol{r}_c) > dV_b(\boldsymbol{r}_c)/2$; $150^o < \theta_p{}^a < 180^o$
Borderline (BD-2)	$d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)/d(-r) = 0$ ($H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 > 0$; $H_b(\boldsymbol{r}_c) < 0$)	$2dG_b(\boldsymbol{r}_c)/d(-r) = -dV_b(\boldsymbol{r}_c)/d(-r)$ ($-V_b(\boldsymbol{r}_c)/2 < G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)$)
CT-TBP with X_3^-	$d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)/d(-r) < 0$ ($H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 > 0$; $H_b(\boldsymbol{r}_c) < 0$)	$2dG_b(\boldsymbol{r}_c)/d(-r) < -dV_b(\boldsymbol{r}_c)/d(-r)$ ($-V_b(\boldsymbol{r}_c)/2 < G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)$)
Borderline (*y*-intercept)	$H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 = 0$ ($H_b(\boldsymbol{r}_c) < 0$)	$G_b(\boldsymbol{r}_c) = -V_b(\boldsymbol{r}_c)/2$ ($G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)$)
Cov-w	$H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 < 0$; $R^c < 0.15$ *au*	$G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)/2$; $R^c < 0.15$ *au*
Borderline (Tentative)	$R^c = 0.15$ *au*	$R^d = 0.15$ *au*
Cov-s	$H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 < 0$; $R^c > 0.15$ *au*	$G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)/2$; $R^d > 0.15$ *au*

[a] $\theta_p = 90^o - \tan^{-1}[dH_b(\boldsymbol{r}_c)/d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)]$, $\theta_p = 125^o$ is tentatively given for $\theta = 90^o$, where θ is defined by $90^o - \tan^{-1}[H_b(\boldsymbol{r}_c)/(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)]$ with $H_b(\boldsymbol{r}_c) = 0$. [b] $\theta_p = 90^o - \tan^{-1}[d(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c))/d(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c)/2)]$, $\theta_p = 125^o$ is tentatively given for $\theta = 90^o$, where θ is defined by $90^o - \tan^{-1}[(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c))/(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c)/2)]$ with $(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c)) = 0$]. [c] $R = [(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)^2 + (H_b(\boldsymbol{r}_c))^2]^{1/2}$. [d] $R = [(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c)/2)^2 + (G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c))^2]^{1/2}$.

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