SUPPORTING INFORMATION FOR

Unconventional Type III halogen···halogen interactions: A quantum mechanical elucidation of σ-hole···σ-hole and di-σ-hole interactions

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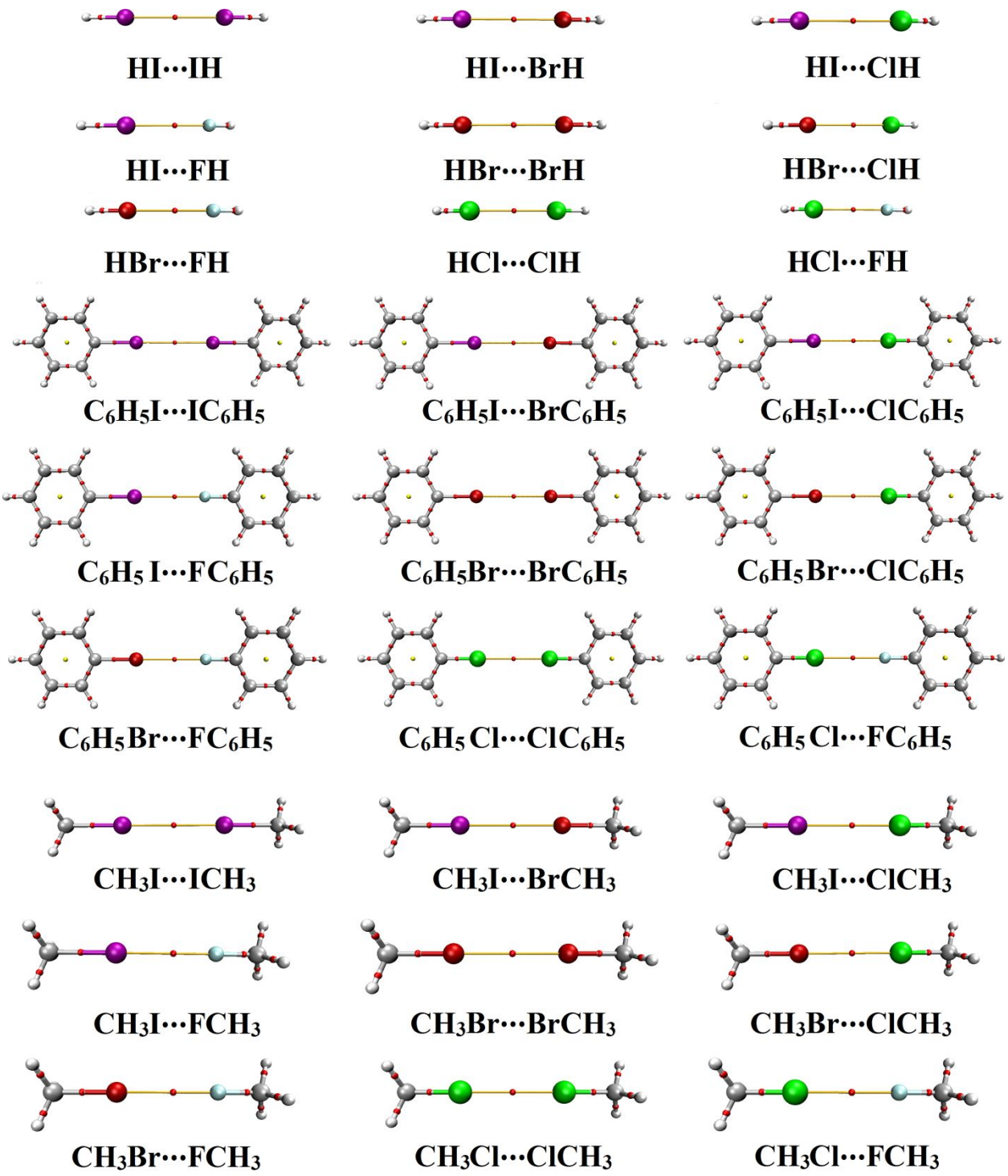

Figure S1. Quantum theory of atoms in molecules (QTAIM) diagrams for HX···XH, $C_6H_5X\cdots XC_6H_5$, and $CH_3X\cdots XCH_3$ (where X= F, Cl, Br, and I) complexes at the most favorable X···X/X' distances. Red dots indicate the locations of bond critical points (BCP) at bond paths (BP) between the two interacting monomers.

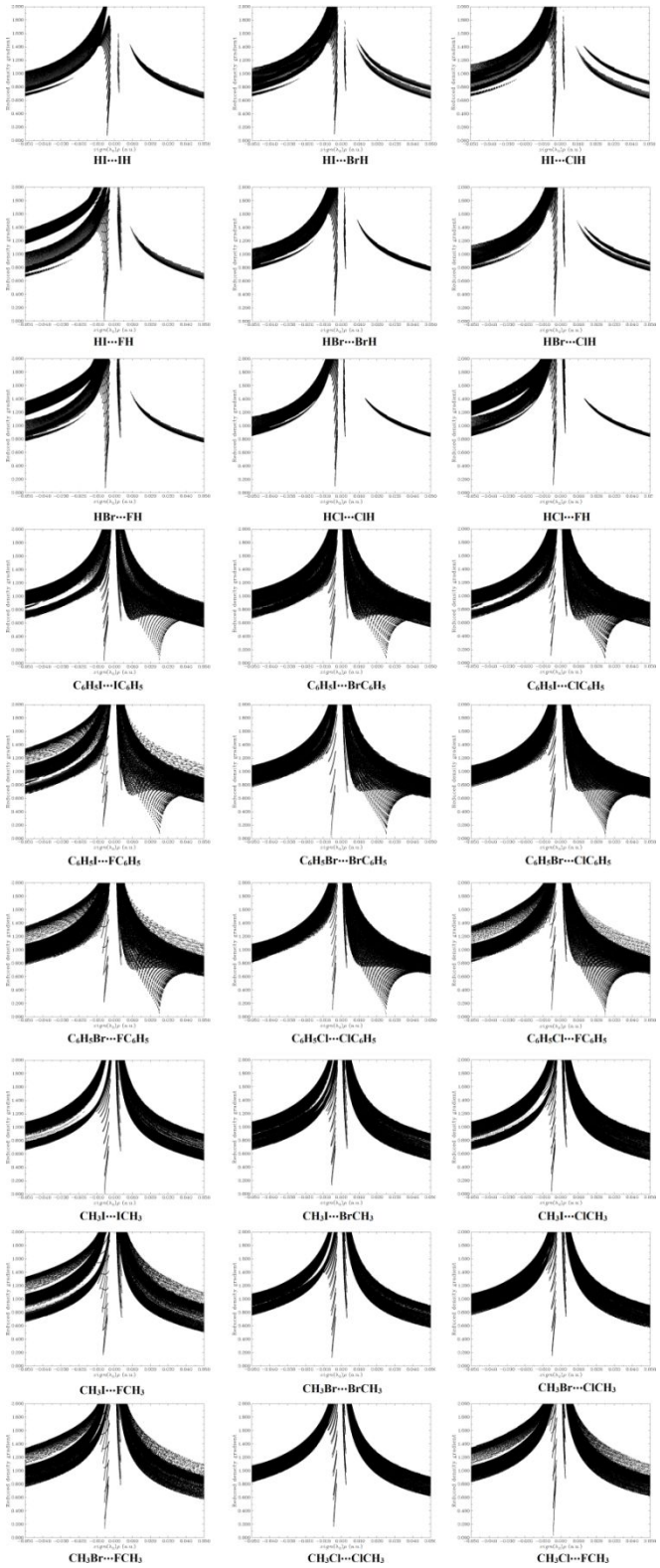

Figure S2. 2D noncovalent interaction (NCI) reduced density gradient (RDG) plots for HX···XH, $C_6H_5X\cdots XC_6H_5$, and $CH_3X\cdots XCH_3$ (where X= F, Cl, Br, and I) complexes at the most favorable X···X/X' distances.

Unconventional Type III halogen···halogen interactions

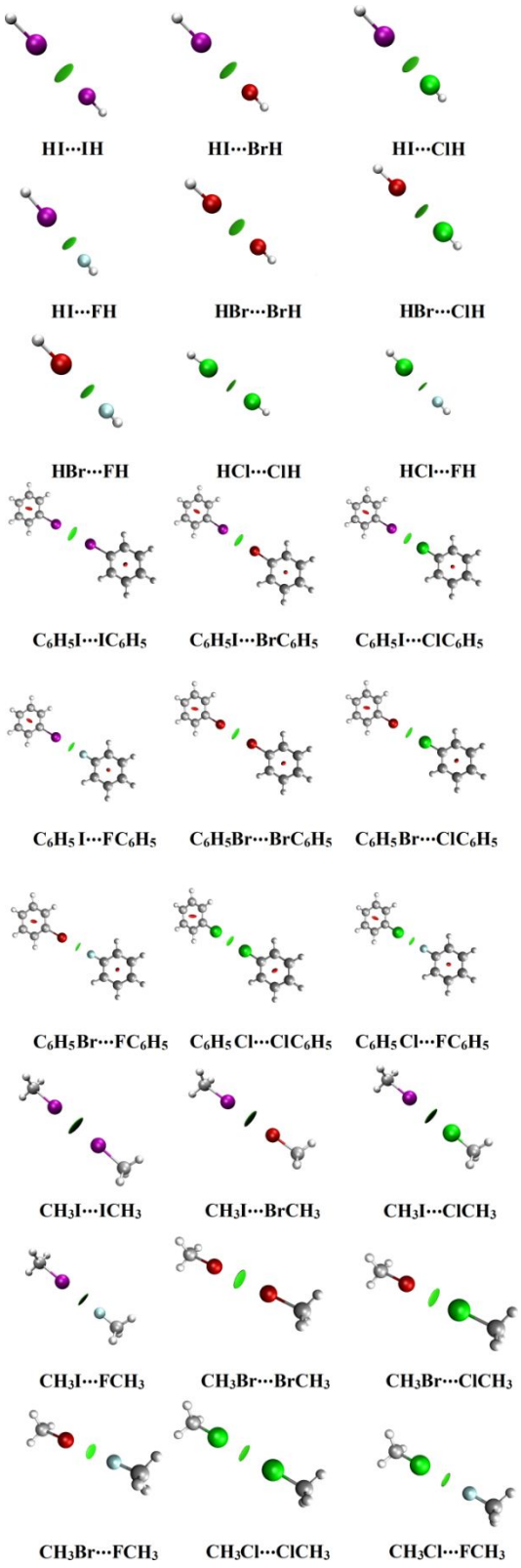

Figure S3. 3D noncovalent interaction (NCI) plots for HX···XH, $C_6H_5X\cdots XC_6H_5$, and $CH_3X\cdots XCH_3$ (where X= F, Cl, Br, and I) complexes at the most favorable X···X/X' distances.

Unconventional Type III halogen···halogen interactions

Table S1. List of hits resulted from CSD survey, including CSD code, measured and absolute halogen···halogen distance (in Å), A-halogen···halogen angle (in degree).

Halogen···halogen System	CSD Code	Halogen···halogen Distance (Å)[a]		A-Halogen···halogen Angle (θ)
		Measured	Absolute	
I···I	AYURES	3.64	0.32	180.00°
Br···Br	BALLAD	3.31	0.39	180.00°
	BTRPYC	3.70	0	180.00°
	CUGSEC	3.41	0.29	180.00°
	KECCED	3.31	0.39	180.00°
	KOGLUQ	3.44	0.26	180.00°
	KOGLUQ01	3.38	0.32	180.00°
	KOGMEB	3.38	0.32	180.00°
	KOGMIF	3.38	0.32	180.00°
	TPHMBR01	3.18	0.52	180.00°
	TPHMBR02	3.19	0.51	180.00°
	JERJIP	3.31	0.39	180.00°
Cl···Cl	ABOSUF01	3.01	0.49	180.00°
	BALKUW	3.23	0.27	180.00°
	BEPZED	3.33	0.17	180.00°
	DANCAW	3.32	0.18	180.00°
	FANVOF	3.15	0.35	179.63°
	HPTBZC	3.41	0.09	180.00°
	JAWDOD	3.15	0.35	179.31°
	OLAWIH	3.19	0.31	179.11°
	SONKUC	3.15	0.35	179.64°
	VICREF	3.20	0.3	180.00°
	XOFFOQ	3.08	0.42	180.00°
	ZZZVTY12	3.21	0.29	180.00°

[a] Absolute distances calculated as difference between the measured distance and the sum of van der Waals radii of the interacted halogen atoms.

Cartesian atomic coordinates

Hydrogen Halide

HI···IH
H -1.60023904 0.00000000 0.00000000
I 0.00000000 0.00000000 0.00000000
H 5.66023880 0.00000000 0.00000000
I 4.06000000 0.00000000 0.00000000

HI···BrH
H -1.40375197 0.00000000 0.00000000
Br 0.00000000 0.00000000 0.00000000
H 5.51023880 0.00000000 0.00000000
I 3.91000000 0.00000000 0.00000000

HI···ClH
H -1.27474201 0.00000000 0.00000000
Cl 0.00000000 0.00000000 0.00000000
H 5.42023880 0.00000000 0.00000000
I 3.82000000 0.00000000 0.00000000

HI···FH
H -0.92183799 0.00000000 -0.00000000
F -0.00000000 -0.00000000 -0.00000000
H 4.90023881 0.00000000 0.00000000
I 3.30000001 0.00000000 0.00000000

HBr···BrH
H -1.40375197 0.00000000 0.00000000
Br 0.00000000 0.00000000 0.00000000
H 5.16375209 0.00000000 0.00000000
Br 3.76000000 0.00000000 0.00000000

HBr···ClH
H -1.40375197 0.00000000 0.00000000
Br 0.00000000 0.00000000 0.00000000
H 4.96474189 0.00000000 0.00000000
Cl 3.69000000 0.00000000 0.00000000

HBr···FH
H -1.40375197 0.00000000 -0.00000000
Br -0.00000000 -0.00000000 -0.00000000
H 4.12183809 0.00000000 0.00000000
F 3.20000005 0.00000000 0.00000000

Unconventional Type III halogen···halogen interactions

HCl···ClH

H	-1.27474201	0.00000000	0.00000000
Cl	0.00000000	0.00000000	0.00000000
H	4.88474189	0.00000000	0.00000000
Cl	3.61000000	0.00000000	0.00000000

HCl···FH

H	-1.27474201	0.00000000	0.00000000
Cl	0.00000000	0.00000000	0.00000000
H	4.13183805	0.00000000	0.00000000
F	3.21000000	0.00000000	0.00000000

Halobenzene

$C_6H_5I\cdots IC_6H_5$

C	-4.16322231	-0.00000665	-1.20547998
C	-2.76919150	-0.00000736	-1.21397328
C	-2.08322096	0.00000000	0.00000000
C	-2.76919341	-0.00000000	1.21396959
C	-4.16322327	-0.00000338	1.20547402
C	-4.86227894	-0.00000267	-0.00000233
H	-4.69991302	-0.00000828	-2.14520216
H	-2.22441101	-0.00000882	-2.14813900
H	-2.22441888	0.00000258	2.14813590
H	-4.69991016	-0.00000083	2.14519882
H	-5.94396782	-0.00000271	0.00000215
I	-0.00000000	0.00000000	0.00000000
C	8.06322241	-0.00000062	-1.20547998
C	6.66919136	-0.00000000	-1.21397340
C	5.98322105	0.00000000	0.00000000
C	6.66919374	0.00000730	1.21396971
C	8.06322384	0.00001064	1.20547390
C	8.76227903	0.00000267	-0.00000234
H	8.59991312	-0.00000471	-2.14520216
H	6.12441111	-0.00000413	-2.14813900
H	6.12441921	0.00001037	2.14813590
H	8.59991026	0.00001377	2.14519882
H	9.84396791	0.00000271	0.00000214
I	3.90000010	0.00000000	0.00000000

$C_6H_5I\cdots BrC_6H_5$

C	-5.66457800	1.20574700	0.00000200
C	-4.27090200	1.21418800	0.00000200
C	-3.58984100	0.00000000	0.00000100
C	-4.27090200	-1.21418700	-0.00000100
C	-5.66457800	-1.20574500	-0.00000100
C	-6.36348600	0.00000000	0.00000000
H	-6.20164700	2.14512400	0.00000200
H	-3.71941500	2.14417100	0.00000300
H	-3.71941700	-2.14417000	-0.00000300
H	-6.20164500	-2.14512400	-0.00000400
H	-7.44507200	-0.00000200	0.00000000
Br	-1.70869500	0.00000000	0.00000000
C	6.20452700	1.20547876	-0.00000124
C	4.81049600	1.21397176	0.00000076
C	4.12452600	-0.00000124	-0.00000224
C	4.81049800	-1.21397124	0.00000176
C	6.20452800	-1.20547524	0.00000476
C	6.90358400	0.00000076	-0.00000124
H	6.74121800	2.14520076	-0.00000324
H	4.26571600	2.14813776	-0.00000124
H	4.26572400	-2.14813724	0.00000276
H	6.74121500	-2.14520024	0.00000476
H	7.98527300	-0.00000424	-0.00000124
I	2.04130500	-0.00000124	-0.00000124

$C_6H_5I\cdots ClC_6H_5$

C	-6.43283650	1.20579020	0.00000561
C	-5.03944150	1.21390720	0.00000061
C	-4.35860150	-0.00000180	-0.00000439
C	-5.03944650	-1.21390880	-0.00000139
C	-6.43284350	-1.20578380	0.00000661
C	-7.13210450	0.00000420	0.00000661
H	-6.96954150	2.14531920	0.00000761
H	-4.48444450	2.14167420	0.00000161
H	-4.48445850	-2.14167880	-0.00000039
H	-6.96954750	-2.14531380	0.00000661
H	-8.21360250	0.00000720	0.00001061
Cl	-2.62235450	-0.00000180	-0.00000439
C	5.22086750	1.20547980	0.00000239
C	3.82683650	1.21397280	0.00000239
C	3.14086550	-0.00000120	-0.00000161
C	3.82683850	-1.21397020	0.00000139
C	5.22086850	-1.20547420	0.00000539
C	5.91992350	0.00000180	0.00000239

Unconventional Type III halogen···halogen interactions

H	5.75755750	2.14520180	0.00000239
H	3.28205550	2.14813780	0.00000139
H	3.28206450	-2.14813720	0.00000039
H	5.75755550	-2.14519920	0.00000539
H	7.00161250	-0.00000220	0.00000239
I	1.05764550	-0.00000120	-0.00000261

$C_6H_5I\cdots FC_6H_5$

C	4.91469200	1.20654513	0.00001043
C	3.52094100	1.21543013	0.00000043
C	2.85461100	0.00000013	-0.00000757
C	3.52094000	-1.21543087	0.00000043
C	4.91469000	-1.20654787	0.00000943
C	5.61292200	-0.00000187	0.00001243
H	5.45222000	2.14531413	0.00001543
H	2.95432200	2.13589213	-0.00000057
H	2.95431800	-2.13589287	-0.00000257
H	5.45221700	-2.14531687	0.00001343
H	6.69420700	-0.00000287	0.00001843
F	1.50480100	0.00000013	-0.00000557
C	-5.92842100	1.20547900	0.00000200
C	-4.53439000	1.21397200	-0.00000100
C	-3.84842000	-0.00000100	0.00000300
C	-4.53439200	-1.21397100	0.00000100
C	-5.92842200	-1.20547500	0.00000000
C	-6.62747800	0.00000100	0.00000400
H	-6.46511200	2.14520100	0.00000300
H	-3.98961000	2.14813800	-0.00000200
H	-3.98961700	-2.14813700	0.00000100
H	-6.46510800	-2.14520000	0.00000200
H	-7.70916600	-0.00000400	0.00000600
I	-1.76519900	-0.00000100	-0.00000100

$C_6H_5Br\cdots BrC_6H_5$

C	-4.01088303	-0.00000346	-1.20574605
C	-2.61720698	-0.00000272	-1.21418798
C	-1.93614595	0.00000000	0.00000000
C	-2.61720698	0.00000000	1.21418703
C	-4.01088303	-0.00000075	1.20574498
C	-4.70979088	-0.00000247	0.00000100
H	-4.54795187	-0.00000579	-2.14512300
H	-2.06572001	-0.00000347	-2.14417100
H	-2.06572192	0.00000134	2.14417005
H	-4.54794901	-0.00000098	2.14512491
H	-5.79137676	-0.00000305	0.00000300

Unconventional Type III halogen···halogen interactions

Br	-0.05500000	0.00000000	0.00000000
C	7.51088303	-0.00000271	1.20574605
C	6.11720722	-0.00000197	1.21418798
C	5.43614595	0.00000000	0.00000000
C	6.11720722	-0.00000076	-1.21418703
C	7.51088303	-0.00000150	-1.20574498
C	8.20979088	-0.00000248	-0.00000100
H	8.04795187	-0.00000446	2.14512300
H	5.56571978	-0.00000214	2.14417100
H	5.56572216	0.00000000	-2.14417005
H	8.04794901	-0.00000232	-2.14512491
H	9.29137676	-0.00000305	-0.00000300
Br	3.55500000	0.00000000	0.00000000

$C_6H_5Br\cdots ClC_6H_5$

C	5.34290000	1.20574695	0.00000292
C	3.94922400	1.21418795	0.00000092
C	3.26816300	-0.00000005	-0.00000108
C	3.94922500	-1.21418705	0.00000092
C	5.34290100	-1.20574405	0.00000192
C	6.04180800	-0.00000005	0.00000392
H	5.87996800	2.14512395	0.00000492
H	3.39773600	2.14417095	0.00000092
H	3.39774000	-2.14417005	-0.00000008
H	5.87996700	-2.14512405	0.00000392
H	7.12339400	-0.00000205	0.00000492
Br	1.38701700	-0.00000105	-0.00000208
C	-5.95346600	1.20578900	0.00000400
C	-4.56007100	1.21390700	-0.00000100
C	-3.87923000	-0.00000300	-0.00000500
C	-4.56007500	-1.21390900	-0.00000100
C	-5.95347200	-1.20578500	0.00000600
C	-6.65273300	0.00000400	0.00000500
H	-6.49017100	2.14531900	0.00000500
H	-4.00507400	2.14167400	-0.00000100
H	-4.00508700	-2.14167900	0.00000000
H	-6.49017700	-2.14531400	0.00000600
H	-7.73423000	0.00000700	0.00000900
Cl	-2.14298300	-0.00000200	-0.00000400

$C_6H_5Br\cdots FC_6H_5$

C	3.19257800	-1.21418820	0.00000368
C	2.51151700	-0.00000020	-0.00000032
C	3.19257800	1.21418680	-0.00000432
C	4.58625400	1.20574480	-0.00000232

Unconventional Type III halogen···halogen interactions

C	5.28516200	0.00000080	0.00000268
H	5.12332300	-2.14512320	0.00000868
H	2.64109100	-2.14417120	0.00000668
H	2.64109300	2.14416980	-0.00000832
H	5.12332000	2.14512480	-0.00000632
H	6.36674800	0.00000280	0.00000368
Br	0.63037100	-0.00000020	-0.00000332
C	-5.93952000	-1.20654600	0.00000200
C	-4.54576900	-1.21543100	-0.00000700
C	-3.87943800	-0.00000100	-0.00001100
C	-4.54576700	1.21543000	0.00000100
C	-5.93951700	1.20654700	0.00001000
C	-6.63775000	0.00000100	0.00000900
H	-6.47704800	-2.14531500	0.00000400
H	-3.97915000	-2.13589300	-0.00001200
H	-3.97914500	2.13589200	0.00000300
H	-6.47704400	2.14531600	0.00001800
H	-7.71903500	0.00000300	0.00001500
F	-2.52962900	-0.00000100	-0.00000900

$C_6H_5Cl\cdots ClC_6H_5$

C	1.20579200	5.93048300	0.00000500
C	1.21391000	4.53708800	-0.00000100
C	0.00000000	3.85624700	-0.00000500
C	-1.21390600	4.53709200	-0.00000100
C	-1.20578200	5.93048900	0.00000700
C	0.00000700	6.62975000	0.00000700
H	2.14532200	6.46718800	0.00000600
H	2.14167600	3.98209000	-0.00000100
H	-2.14167700	3.98210500	0.00000000
H	-2.14531100	6.46719400	0.00000800
H	0.00001000	7.71124800	0.00001200
Cl	0.00000000	2.12000000	-0.00000500
C	-1.20579200	-5.16048300	0.00000500
C	-1.21391000	-3.76708800	-0.00000100
C	0.00000000	-3.08624700	-0.00000500
C	1.21390600	-3.76709200	-0.00000100
C	1.20578200	-5.16048900	0.00000700
C	-0.00000700	-5.85975000	0.00000700
H	-2.14532200	-5.69718800	0.00000600
H	-2.14167600	-3.21209000	-0.00000100
H	2.14167700	-3.21210500	0.00000000
H	2.14531100	-5.69719400	0.00000800
H	-0.00001000	-6.94124800	0.00001200
Cl	0.00000000	-1.35000000	-0.00000500

Unconventional Type III halogen···halogen interactions

$C_6H_5Cl\cdots FC_6H_5$

C	-5.09406200	1.20578900	0.00001300
C	-3.70066700	1.21390700	0.00000600
C	-3.01982500	-0.00000200	-0.00000600
C	-3.70067000	-1.21390900	-0.00000800
C	-5.09406700	-1.20578500	0.00000100
C	-5.79332800	0.00000300	0.00000800
H	-5.63076700	2.14531800	0.00002100
H	-3.14567000	2.14167400	0.00001100
H	-3.14568200	-2.14167900	-0.00001300
H	-5.63077200	-2.14531500	-0.00000300
H	-6.87482700	0.00000600	0.00001400
Cl	-1.28357900	-0.00000200	-0.00000700
C	5.26631200	1.20654704	0.00000096
C	3.87256100	1.21543104	-0.00000904
C	3.20623000	0.00000104	-0.00001104
C	3.87256000	-1.21542996	0.00000396
C	5.26631000	-1.20654596	0.00001396
C	5.96454200	0.00000004	0.00001096
H	5.80383900	2.14531604	0.00000096
H	3.30594100	2.13589304	-0.00001704
H	3.30593900	-2.13589296	0.00000696
H	5.80383700	-2.14531496	0.00002496
H	7.04582700	-0.00000196	0.00001796
F	1.85642100	0.00000004	-0.00001004

<u>Halomethane</u>

$CH_3I\cdots ICH_3$

C	-2.12287211	0.00000000	0.00000000
H	-2.45246005	0.00000000	1.03174102
H	-2.45246005	-0.89351404	-0.51586998
H	-2.45246005	0.89351398	-0.51586998
I	0.00000000	0.00000000	0.00000000
C	6.06287188	0.00000000	0.00000000
H	6.39245981	-0.89351416	0.51587009
H	6.39245981	0.89351326	0.51587123
H	6.39245981	0.00000000	-1.03174078
I	3.94000000	0.00000000	0.00000000

$CH_3I\cdots BrCH_3$

C	-1.92430401	0.00000000	0.00000000
H	-2.25771689	0.00000000	1.03069699

Unconventional Type III halogen···halogen interactions

H	-2.25771689	-0.89261001	-0.51534897
H	-2.25771689	0.89261001	-0.51534897
Br	0.00000000	0.00000000	0.00000000
C	5.91287188	0.00000000	0.00000000
H	6.24245981	0.00000000	-1.03174102
H	6.24245981	-0.89351398	0.51586998
H	6.24245981	0.89351398	0.51586998
I	3.79000000	0.00000000	0.00000000

$CH_3I\cdots ClCH_3$

C	-1.78047502	0.00000000	0.00000000
H	-2.12192202	0.00000000	1.02879500
H	-2.12192202	-0.89096200	-0.51439703
H	-2.12192202	0.89096200	-0.51439703
Cl	0.00000000	0.00000000	0.00000000
C	5.83287188	0.00000000	0.00000000
H	6.16245981	0.00000034	-1.03174102
H	6.16245981	-0.89351416	0.51586968
H	6.16245981	0.89351386	0.51587027
I	3.71000000	0.00000000	0.00000000

$CH_3I\cdots FCH_3$

C	-1.38842297	0.00000000	0.00000000
H	-1.73670304	0.00000000	1.02973104
H	-1.73670304	-0.89177299	-0.51486498
H	-1.73670304	0.89177299	-0.51486498
F	0.00000000	0.00000000	0.00000000
C	5.40287188	0.00000000	0.00000000
H	5.73245981	-0.00000014	-1.03174102
H	5.73245981	-0.89351392	0.51587009
H	5.73245981	0.89351410	0.51586986
I	3.28000000	0.00000000	0.00000000

$CH_3Br\cdots BrCH_3$

C	-1.92430401	0.00000000	0.00000000
H	-2.25771689	0.00000000	1.03069699
H	-2.25771689	-0.89260995	-0.51534897
H	-2.25771689	0.89260995	-0.51534903
Br	0.00000000	0.00000000	0.00000000
C	5.57430401	0.00000000	0.00000000
H	5.90771713	-0.89260966	0.51534879
H	5.90771713	0.89261049	0.51534820
H	5.90771713	0.00000000	-1.03069746
Br	3.65000000	0.00000000	0.00000000

Unconventional Type III halogen···halogen interactions

$CH_3Br\cdots ClCH_3$

C	-1.92430401	0.00000000	0.00000000
H	-2.25771689	0.00000000	1.03069699
H	-2.25771689	-0.89261001	-0.51534897
H	-2.25771689	0.89261001	-0.51534897
Br	0.00000000	0.00000000	0.00000000
C	5.36047514	0.00000000	0.00000000
H	5.70192202	-0.89096242	0.51439780
H	5.70192202	0.89096200	0.51439697
H	5.70192202	-0.00000046	-1.02879429
Cl	3.58000000	0.00000000	0.00000000

$CH_3Br\cdots FCH_3$

C	-1.92430401	-0.00000000	0.00000000
H	-2.25771689	0.00000000	1.03069699
H	-2.25771689	-0.89261001	-0.51534897
H	-2.25771689	0.89261001	-0.51534897
Br	-0.00000000	0.00000000	0.00000000
C	4.58842301	0.00000000	0.00000000
H	4.93670297	-0.89177322	0.51486552
H	4.93670297	0.89177269	0.51486558
H	4.93670297	-0.00000034	-1.02973056
F	3.20000005	0.00000000	0.00000000

$CH_3Cl\cdots ClCH_3$

C	-1.78047502	0.00000000	0.00000000
H	-2.12192202	0.00000000	1.02879500
H	-2.12192202	-0.89096200	-0.51439703
H	-2.12192202	0.89096200	-0.51439703
Cl	0.00000000	0.00000000	0.00000000
C	5.32047514	0.00000000	0.00000000
H	5.66192202	0.00000000	-1.02879500
H	5.66192202	-0.89096200	0.51439703
H	5.66192202	0.89096200	0.51439703
Cl	3.54000000	0.00000000	0.00000000

$CH_3Cl\cdots FCH_3$

C	-1.78047502	0.00000000	0.00000000
H	-2.12192202	0.00000000	1.02879500
H	-2.12192202	-0.89096200	-0.51439703
H	-2.12192202	0.89096200	-0.51439703
Cl	0.00000000	0.00000000	0.00000000
C	4.61842297	0.00000000	0.00000000
H	4.96670292	0.00000020	-1.02973104
H	4.96670292	-0.89177310	0.51486480

Unconventional Type III halogen···halogen interactions

H	4.96670292	0.89177293	0.51486516
F	3.23000000	0.00000000	0.00000000