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JOURNAL OF PHYSICAL CHEMISTRY

Supporting Information

JP004035S

SUPPLEMENTARY MATERIAL

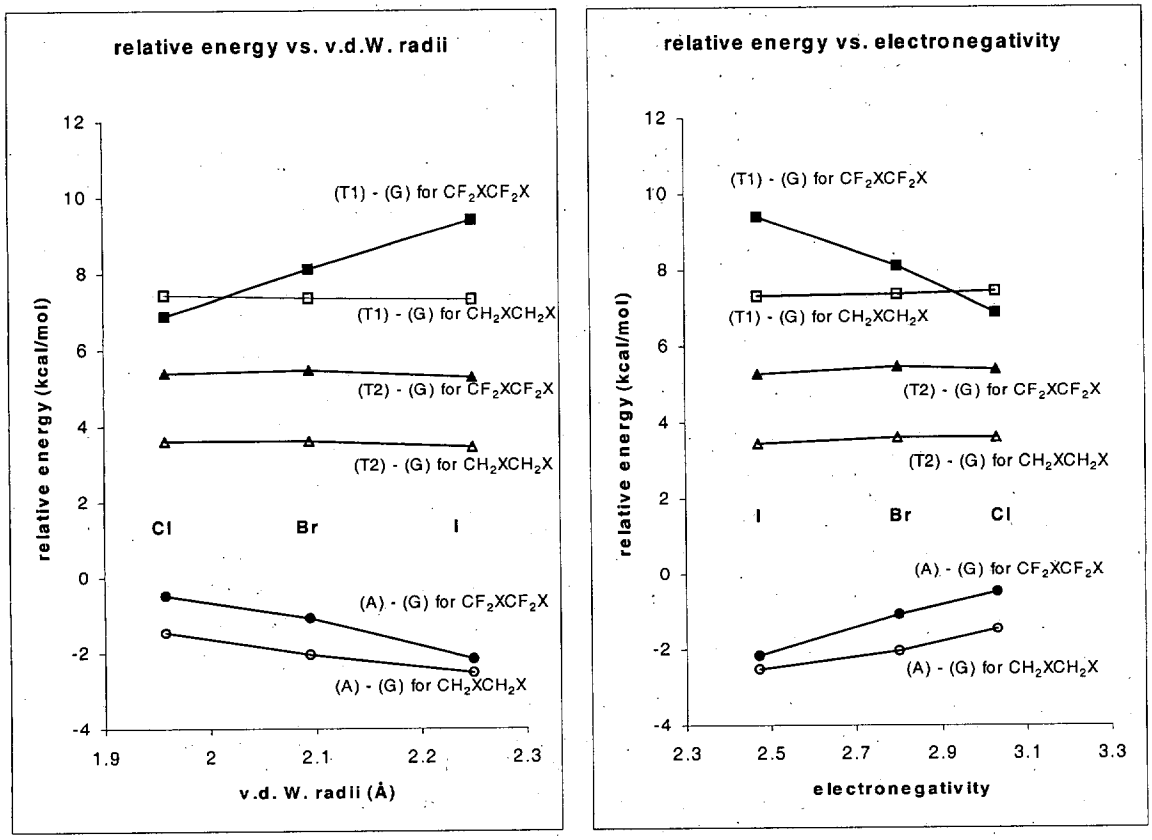

Figure S1. Correlation between the van der Waalls radii or group electronegativity and the relative energy differences.

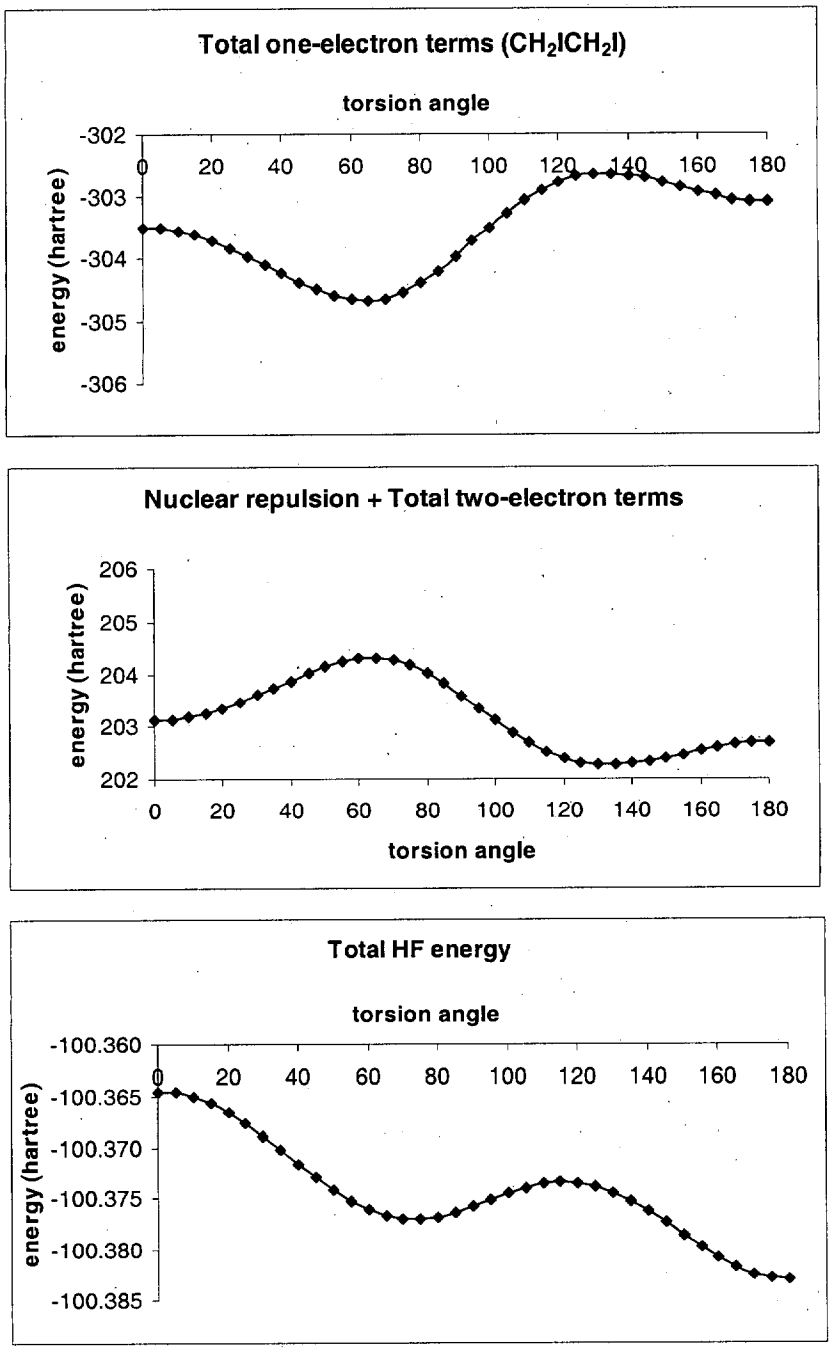

Figure S2. Energy decomposition for CH_2ICH_2I calculated at HF (LAV3P) level. Total HF energy is sum of the attractive energy (Total one-electron term) and repulsive energy (Nuclear repulsion + Total two-electron terms). The energy is in hartrees and the angles are in degrees.

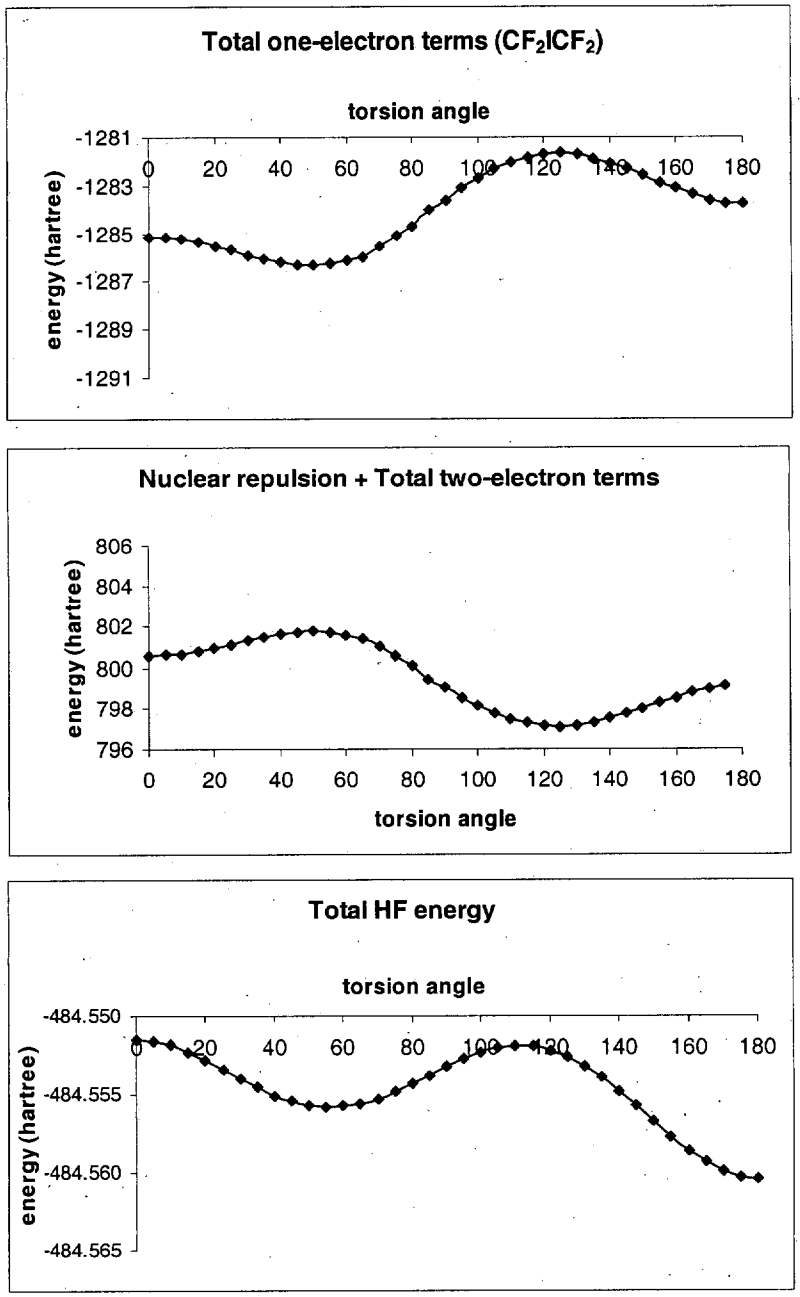

Figure S3. Energy decomposition for CF_2ICF_2 calculated at HF (LAV3P) level. Total HF energy is sum of the attractive energy (Total one-electron term) and repulsive energy (Nuclear repulsion + Total two-electron terms). The energy is in hartrees and the angles are in degrees.

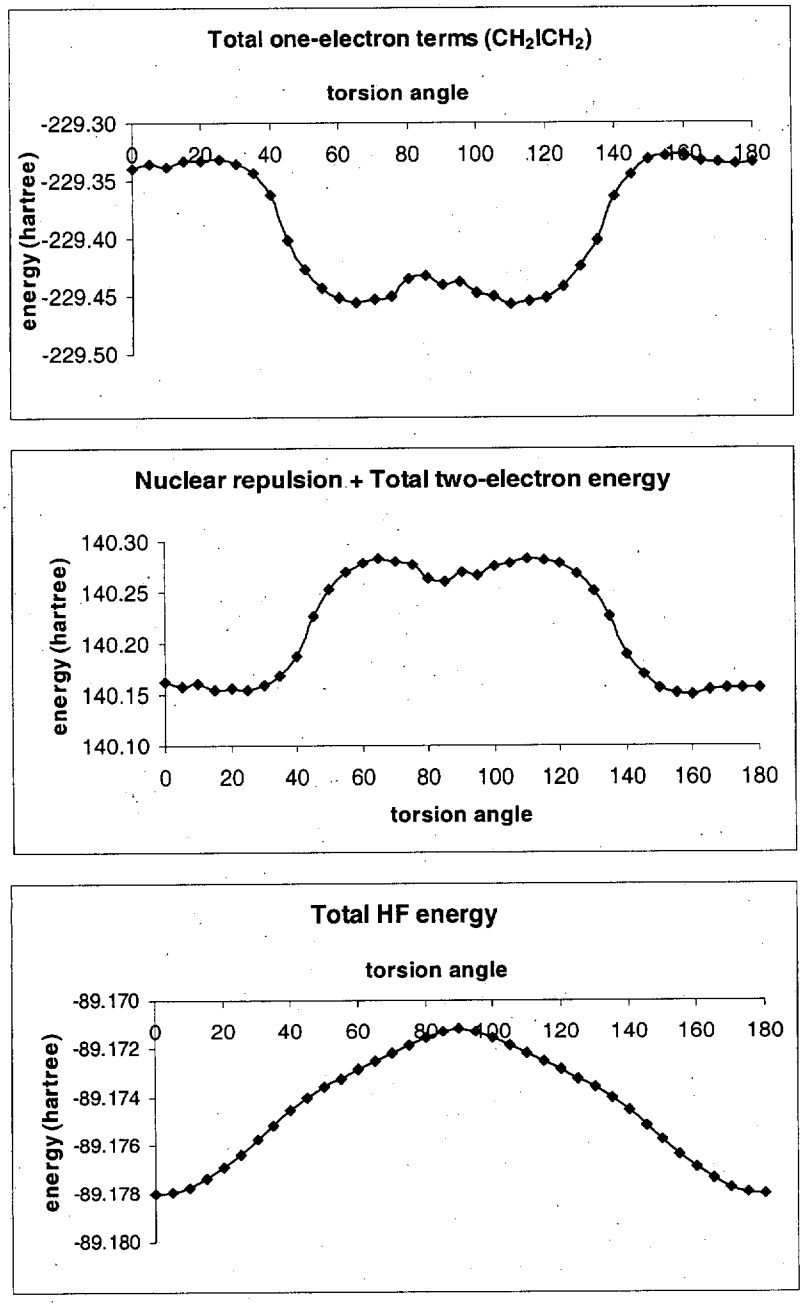

Figure S4. Energy decomposition for CH_2ICH_2 calculated at HF (LAV3P) level. Total HF energy is sum of the attractive energy (Total one-electron term) and repulsive energy (Nuclear repulsion + Total two-electron terms). The energy is in hartrees and the angles are in degrees.

Table S1a. The structural parameters of the CF_2XCF_2X and CF_2XCF_2• radicals (X = I, Br and Cl) optimized at HF (LAV3P) level of theory. The bond length is given in angstrom and the angle is in degree. The prefix A-, G-, and T- mean anti-, gauche-, and transition state, respectively. *a* corresponds to the C-C bond, *b, c, d* and *e* correspond to C-F bonds, and *f* and *g* corresponds to C-X bonds.

X = I (HF (LAV3P))

	CF_2ICF_2I						CF_2ICF_2•			
	A		G		T1	T2	A	G	T1	T2
	HF	Expt[a]	HF	Expt[a]	HF	HF	HF	HF	HF	HF
a	1.531	1.540 (13)	1.537	1.540 (13)	1.583	1.570	1.502	1.508	1.522	1.524
b	1.319	1.328 (3)	1.323	1.328 (3)	1.321	1.319	1.320	1.326	1.320	1.322
c	1.319		1.319		1.320	1.319	1.320	1.321	1.320	1.326
d	1.319		1.323		1.321	1.319	1.304	1.309	1.306	1.306
e	1.319		1.319		1.320	1.319	1.304	1.307	1.306	1.305
f	2.169	2.139 (7)	2.159	2.139 (7)	2.167	2.170				
g	2.169		2.159		2.167	2.170	2.180	2.162	2.173	2.168
ab	109.0	109.4 (10)	106.2	109.4 (10)	107.3	108.1	108.5	109.6	109.9	109.2
ac	109.0		108.6		107.3	110.8	108.5	108.0	109.9	107.9
ad	109.0		106.2		107.3	108.1	114.0	112.2	113.7	113.2
ae	109.0		108.6		107.3	110.8	114.0	113.8	113.7	116.9
af	112.0	111.6 (10)	115.0	111.6 (10)	119.9	114.2				
ag	112.0		115.0		119.9	114.2	113.0	112.1	110.9	114.6
bc	108.7	107.8 (10)	108.0	107.8 (10)	107.6	107.2	108.8	108.0	108.5	107.4
bg	109.1		108.7		107.1	108.7	108.8	109.5	108.8	109.0
cg	109.1		109.9		107.1	107.8	108.8	109.5	108.8	108.4
de	108.7		108.0		107.6	107.2	111.8	111.3	111.7	110.9
df	109.1		108.7		107.1	108.7				
ef	109.1		109.9		107.1	107.8				
bad	61.5		-52.1		-114.9	0.1	55.9	-65.6	-124.5	-11.3
bae	180.0		63.9		0.5	117.2	-174.0	61.9	4.9	119.4
baf	-59.3		-172.4		122.8	-120.9				
cad	180.0		63.9		0.5	117.2	174.0	51.8	-5.1	105.2
cae	-61.5		179.9		115.9	-125.7	-55.9	179.4	124.3	-124.1
caf	59.3		-56.4		-121.8	-3.8				
gad	-59.3		-172.4		122.8	-120.9	-65.0	172.6	115.2	-133.9
gae	59.3		-56.4		-121.8	-3.8	65.0	-59.9	-115.4	-3.3
gaf	180.0	180 (fixed)	67.3	70 (3)	0.5	118.1				

a) Electron diffraction data[23]

X = Br (HF (LAV3P))

	CF_2BrCF_2Br						CF_2BrCF_2•			
	A		G		T1	T2	A	G	T1	T2
	HF	Expt[a]	HF	Expt[a]	HF	HF	HF	HF	HF	HF
a	1.531	1.557 (13)	1.536	1.557 (13)	1.578	1.570	1.502	1.508	1.521	1.524
b	1.312	1.334 (3)	1.317	1.334 (3)	1.315	1.314	1.315	1.320	1.314	1.316
c	1.312		1.313		1.315	1.312	1.315	1.316	1.314	1.321
d	1.312		1.317		1.315	1.314	1.303	1.308	1.305	1.305
e	1.312		1.313		1.315	1.312	1.303	1.305	1.305	1.302
f	1.976	1.925 (5)	1.966	1.925 (5)	1.970	1.975				
g	1.976		1.966		1.970	1.975	1.989	1.973	1.985	1.976
ab	109.5	109.9 (4)	106.8	109.9 (4)	107.8	108.2	109.1	110.4	110.5	109.8
ac	109.5		109.3		107.8	111.4	109.1	108,7	110.5	108.5
ad	109.5		106.8		107.8	108.2	113.9	112.0	113.5	112.9
ae	109.5		109.3		107.8	111.4	113.9	113.8	113.6	116.9
af	110.7	110.5 (5)	113.4	110.5 (5)	117.8	112.9				
ag	110.7		113.4		117.8	112.9	111.9	110.8	109.8	113.4
bc	109.3	108.4 (8)	108.6	108.4 (8)	108.2	107.8	109.3	108.5	109.0	107.9
bg	109.0		108.8		107.5	108.5	108.7	109.1	108.5	108.8
cg	109.0		109.8		107.5	108.0	108.7	109.3	108.5	108.3
de	109.3		108.6		108.2	108.0	108.7	111.5	111.8	111.1
df	109.0		108.8		107.5	108.0				
ef	109.0		109.8		107.5	108.5				
bad	60.2		-54.3		-116.5	-1.2	55.3	-66.9	-125.0	-11.3
bae	180.0		63.0		0.0	117.2	-174.6	60.7	4.2	119.3
baf	-59.9		-174.1		121.8	-121.2				
cad	180.0		63.0		0.0	117.2	174.6	52.1	-4.3	106.4
cae	-60.2		179.7		116.5	-124.5	-55.3	179.6	124.9	-122.9
caf	59.9		-56.8		-121.7	-2.8				
gad	-59.9		-174.1		121.8	-121.2	-65.1	172.2	115.4	-133.3
gae	59.9		-56.8		-121.7	-2.8	65.1	-60.3	-115.4	-2.6
gaf	180.0	180 (fixed)	66.0	67 (3)	0.0	118.8				

a) Electron diffraction data[23]

X = Cl (HF (LAV3P))

	CF_2ClCF_2Cl						CF_2ClCF_2•			
	A		G		T1	T2	A	G	T1	T2
	HF	Expt[b]	HF	Expt[b]	HF	HF	HF	HF	HF	HF
a	1.533	1.563 (7)	1.536	1.563 (7)	1.576	1.572	1.504	1.508	1.523	1.525
b	1.310	1.331 (2)	1.314	1.331 (2)	1.313	1.312	1.313	1.318	1.313	1.314
c	1.310		1.311		1.313	1.310	1.313	1.314	1.313	1.319
d	1.310		1.314		1.313	1.312	1.303	1.307	1.305	1.305
e	1.310		1.311		1.313	1.310	1.303	1.304	1.305	1.302
f	1.783	1.748 (3)	1.776	1.748 (3)	1.777	1.782				
g	1.783		1.776		1.777	1.782	1.797	1.783	1.793	1.786
ab	109.4	108.9 (3)	107.1	108.9 (3)	108.1	108.3	109.3	110.6	110.6	110.0
ac	109.4		109.3		108.1	111.2	109.3	108.8	110.5	108.7
ad	109.4		107.1		108.1	108.3	113.6	111.9	113.5	112.9
ae	109.4		109.3		108.1	111.2	113.6	113.7	113.5	116.5
af	110.3	110.7 (4)	112.8	110.7 (4)	116.2	112.3				
ag	110.3		112.8		116.2	112.4	111.6	110.8	110.0	113.0
bc	109.5	108.7 (3)	108.9	108.7 (3)	108.4	108.2	109.3	108.6	109.0	108.1
bg	109.1		109.0		108.0	108.4	108.6	108.9	108.3	108.8
cg	109.1		109.7		108.0	108.2	108.6	109.2	108.3	108.2
de	109.5		108.9		108.4	108.2	112.0	111.6	111.8	111.3
df	109.1		109.0		108.0	108.4				
ef	109.1		109.7		108.0	108.2				
bad	60.0		-55.7		-117.2	-0.8	55.4	-65.9	-125.1	-9.6
bae	180.0		62.1		-0.1	118.0	-175.0	61.7	4.0	121.1
baf	-60.0		-175.5		121.4	-120.6				
cad	180.0		62.1		-0.1	118.0	175.0	53.3	-4.3	108.5
cae	-60.0		180.0		117.0	-123.2	-55.4	-179.1	124.8	-120.8
caf	60.0		-57.7		-121.5	-1.8				
gad	-60.0		-175.5		121.4	-120.6	-64.8	173.3	115.3	-131.3
gae	60.0		-57.7		-121.5	-1.8	64.8	-59.1	-115.6	-0.7
gaf	180.0	180 (fixed)	64.6	62.5 (13)	-0.1	119.7				

b) Electron diffraction data[30]

Table S1b. The structural parameters of the CF_2XCF_2X and CF_2XCF_2• radicals (X = I, Br and Cl) optimized at HF (LAV3P) level of theory. The bond length is given in angstrom and the angle is in degree. The prefix A-, G-, and T- mean anti-, gauche-, and transition state, respectively. *a* corresponds to the C-C bond, *b, c, d* and *e* correspond to C-F bonds, and *f* and *g* corresponds to C-X bonds.

X = I (HF (LAV3P(d)))

	CF_2ICF_2I				CF_2ICF_2•			
	A	G	T1	T2	A	G	T1	T2
a	1.532	1.540	1.584	1.573	1.503	1.508	1.523	1.525
b	1.320	1.324	1.322	1.320	1.322	1.327	1.321	1.323
c	1.320	1.321	1.322	1.321	1.322	1.323	1.321	1.328
d	1.320	1.324	1.322	1.320	1.304	1.309	1.307	1.306
e	1.320	1.321	1.322	1.321	1.304	1.307	1.307	1.305
f	2.159	2.147	2.153	2.157				
g	2.159	2.147	2.153	2.157	2.164	2.149	2.159	2.154
ab	109.0	106.4	107.3	108.0	108.6	109.8	110.0	109.3
ac	109.0	108.7	107.3	110.7	108.6	108.1	110.0	107.9
ad	109.0	106.4	107.3	108.0	114.0	112.3	113.7	113.1
ae	109.0	108.7	107.3	110.7	114.0	113.8	113.7	117.0
af	111.9	114.8	119.7	114.2				
ag	111.9	114.8	119.7	114.2	112.7	111.8	110.6	114.5
bc	108.7	107.9	107.5	107.1	108.7	108.0	108.4	107.3
bg	109.1	110.1	107.3	108.6	109.1	109.6	109.0	109.1
cg	109.1	108.7	107.2	107.9	109.1	109.6	109.0	108.5
de	108.7	107.9	107.5	107.1	111.8	111.2	111.7	110.8
df	109.1	108.7	107.3	108.6				
ef	109.1	110.1	107.2	107.2				
bad	61.5	-51.6	-115.3	-0.4	56.0	-66.1	-124.2	-11.1
bae	180.0	64.3	0.0	116.5	-174.0	61.4	5.0	119.5
baf	-59.3	-171.9	122.3	-121.4				
cad	180.0	64.3	0.0	116.5	174.0	51.4	-5.0	105.3
cae	-61.5	-179.7	115.4	-126.6	-56.0	178.9	124.3	-124.1
caf	59.3	-56.0	-122.3	-4.5				
gad	-59.3	-171.9	122.4	-121.4	-65.0	172.1	115.4	-133.7
gae	59.3	-56.0	-122.3	-4.5	65.0	-60.4	-115.3	-3.1
gaf	180.0	67.8	0.0	117.6				

X = Br (HF (LAV3P(d)))

	CF_2BrCF_2Br				$CF_2BrCF_2•$			
	A	G	T1	T2	A	G	T1	T2
a	1.536	1.540	1.583	1.576	1.505	1.509	1.524	1.527
b	1.316	1.321	1.318	1.317	1.319	1.323	1.318	1.320
c	1.316	1.316	1.318	1.316	1.319	1.319	1.318	1.324
d	1.316	1.321	1.318	1.317	1.304	1.309	1.306	1.306
e	1.316	1.316	1.318	1.316	1.304	1.306	1.306	1.303
f	1.944	1.935	1.939	1.943				
g	1.944	1.935	1.939	1.943	1.952	1.940	1.949	1.943
ab	109.2	106.7	107.6	108.0	108.8	110.2	110.2	109.5
ac	109.2	109.0	107.6	111.1	108.8	108.5	110.2	108.2
ad	109.2	106.7	107.6	108.0	113.9	112.1	113.6	113.0
ae	109.2	109.0	107.6	111.1	113.9	113.8	113.6	116.9
af	111.1	113.6	117.6	113.1				
ag	111.1	113.6	117.6	113.1	112.1	111.0	110.1	113.6
bc	108.9	108.2	107.8	107.4	108.8	108.1	108.5	107.5
bg	109.2	109.0	107.9	108.8	109.1	109.4	108.9	109.2
cg	109.2	110.1	107.9	108.2	109.1	109.6	108.9	108.6
de	108.9	108.2	107.8	107.4	112.0	111.4	111.7	111.0
df	109.2	109.0	107.9	108.8				
ef	109.2	110.1	107.9	108.2				
bad	61.1	-53.8	-115.9	0.4	55.8	-66.5	-124.4	-9.6
bae	180.0	62.9	0.0	118.0	-174.2	61.0	4.6	121.2
baf	-59.5	-173.9	122.0	-120.0				
cad	180.0	62.9	0.0	118.0	174.2	51.7	-4.8	107.4
cae	-61.1	179.6	116.0	-124.4	-55.8	179.2	124.3	-121.9
caf	59.5	-57.2	-122.0	-2.4				
gad	-59.5	-173.9	122.0	-120.0	-65.0	172.1	115.5	-131.9
gae	59.5	-57.2	-122.0	-2.4	65.0	-60.4	-115.5	-1.2
gaf	180.0	65.9	0.0	119.5				

X = Cl (HF (LAV3P(d)))

	CF_2ClCF_2Cl				CF_2ClCF_2•			
	A	G	T1	T2	A	G	T1	T2
a	1.538	1.540	1.581	1.577	1.507	1.510	1.526	1.528
b	1.316	1.319	1.317	1.317	1.319	1.324	1.319	1.320
c	1.316	1.316	1.318	1.316	1.319	1.319	1.319	1.324
d	1.316	1.319	1.317	1.317	1.304	1.307	1.306	1.306
e	1.316	1.316	1.318	1.316	1.304	1.306	1.306	1.304
f	1.743	1.739	1.741	1.743				
g	1.743	1.739	1.741	1.743	1.752	1.744	1.751	1.745
ab	108.9	106.9	107.8	108.1	108.6	110.0	110.0	109.5
ac	108.9	108.8	107.8	110.7	108.6	108.3	110.0	108.2
ad	108.9	106.9	107.8	108.1	113.6	112.1	113.6	113.2
ae	108.9	108.8	107.8	110.7	113.6	113.7	113.6	116.4
af	111.0	113.1	116.2	112.7				
ag	111.0	113.1	116.2	112.7	112.2	111.2	110.6	113.3
bc	108.9	108.4	107.9	107.6	108.7	108.0	108.4	107.5
bg	109.5	109.4	108.4	109.0	109.3	109.4	108.9	109.3
cg	109.5	110.1	108.5	108.6	109.3	109.7	108.9	108.8
de	108.9	108.4	107.8	107.6	111.8	111.5	111.6	111.1
df	109.5	109.4	108.5	109.0				
ef	109.5	110.1	108.5	108.6				
bad	61.4	-55.1	-116.3	1.3	56.3	-64.7	-124.4	-7.8
bae	180.0	61.8	-0.1	118.8	-174.4	62.9	4.6	122.8
baf	-59.3	-175.6	121.8	-119.3				
cad	180.0	61.8	-0.1	118.9	174.4	53.2	-5.1	109.1
cae	-61.4	178.6	116.1	-123.6	-56.3	179.2	123.9	-120.3
caf	59.3	-58.7	-121.9	-1.7				
gad	-59.3	-175.6	121.8	-119.3	-64.6	173.9	115.3	-130.1
gae	59.3	-58.7	-122.0	-1.7	64.6	-58.6	-115.7	0.4
gaf	180.0	64.0	0.0	120.2				

Table S1c. The structural parameters of the CF_2XCF_2X and CF_2XCF_2• radicals (X = I, Br and Cl) optimized at B3PW91 (LAV3P) level of theory. The bond length is given in angstrom and the angle is in degree. The prefix A-, G-, and T- mean anti-, gauche-, and transition state, respectively. *a* corresponds to the C-C bond, *b, c, d* and *e* correspond to C-F bonds, and *f* and *g* corresponds to C-X bonds.

X = I (B3PW91 (LAV3P))

	CF_2ICF_2I						CF_2ICF_2•			
	A		G		T1	T2	A	G	T1	T2
	HF	Expt[a]	HF	Expt[a]	HF	HF	HF	HF	HF	HF
a	1.545	1.540 (13)	1.555	1.540 (13)	1.604	1.589	1.489	1.510	1.512	1.523
b	1.333	1.328 (3)	1.340	1.328 (3)	1.336	1.335	1.334	1.347	1.337	1.342
c	1.333		1.334		1.336	1.333	1.334	1.337	1.337	1.343
d	1.333		1.340		1.336	1.333	1.315	1.322	1.323	1.323
e	1.333		1.334		1.336	1.333	1.315	1.326	1.323	1.318
f	2.207	2.139 (7)	2.193	2.139 (7)	2.197	2.204				
g	2.207		2.193		2.197	2.204	2.266	2.201	2.226	2.208
ab	109.7	109.4 (10)	106.7	109.4 (10)	107.2	108.0	110.1	111.5	110.8	19.9
ac	109.7		109.4		107.2	111.5	110.1	108.5	110.8	108.9
ad	109.7		106.7		107.2	108.0	116.1	113.3	114.8	113.3
ae	109.7		109.4		107.2	111.5	116.1	115.2	114.8	118.5
af	110.4	111.6 (10)	113.3	111.6 (10)	118.8	112.9				
ag	110.4		113.3		118.8	112.9	111.3	110.2	109.8	113.1
bc	109.4	107.8 (10)	108.5	107.8 (10)	108.3	107.9	110.0	108.2	109.5	107.5
bg	108.8		108.9		107.5	108.7	107.6	108.9	108.0	109.3
cg	108.8		109.9		107.5	107.7	107.6	109.4	108.0	108.0
de	109.4		108.5		108.3	107.9	112.8	111.8	112.7	111.5
df	108.8		108.9		107.5	108.7				
ef	108.8		109.9		107.5	107.7				
bad	59.8		-52.5		-116.1	-0.4	51.2	-68.7	-127.8	-21.6
bae	180.0		64.6		0.0	118.0	-172.7	61.7	5.3	111.9
baf	-60.1		-172.3		122.0	-120.5				
cad	180.0		64.6		0.0	118.0	172.7	50.3	-6.0	95.9
cae	-59.8		-178.2		116.1	-123.6	-51.2	-179.2	127.1	-130.7
caf	60.1		-55.2		-121.9	-2.2				
gad	-60.1		-172.3		122.0	-120.5	-68.0	170.1	113.1	-144.0
gae	60.1		-55.2		-121.9	-2.2	68.0	-59.4	-113.8	-10.5
gaf	180.0	180 (fixed)	67.8	70 (3)	0.0	119.3				

a) Electron diffraction data[23]

X = Br (B3PW91 (LAV3P))

	CF_2BrCF_2Br						$CF_2BrCF_2•$			
	A		G		T1	T2	A	G	T1	T2
	HF	Expt[a]	HF	Expt[a]	HF	HF	HF	HF	HF	HF
a	1.547	1.557 (13)	1.553	1.557 (13)	1.598	1.589	1.493	1.510	1.513	1.523
b	1.329	1.334 (3)	1.335	1.334 (3)	1.332	1.331	1.331	1.342	1.333	1.337
c	1.329		1.330		1.332	1.327	1.331	1.333	1.333	1.339
d	1.329		1.335		1.332	1.331	1.316	1.326	1.322	1.323
e	1.329		1.330		1.332	1.327	1.316	1.321	1.322	1.317
f	2.011	1.925 (5)	1.997	1.925 (5)	1.999	2.007				
g	2.011		1.997		1.999	2.007	2.063	2.009	2.031	2.013
ab	110.0	109.9 (4)	107.3	109.9 (4)	107.7	108.2	110.3	112.1	111.1	110.3
ac	110.0		109.9		107.7	111.9	110.3	109.0	111.1	109.4
ad	110.0		107.3		107.7	108.2	115.8	113.2	114.7	113.1
ae	110.0		109.9		107.7	111.9	115.8	115.2	114.8	118.4
af	109.6	110.5 (5)	112.1	110.5 (5)	116.9	111.8				
ag	109.6		112.1		116.9	111.8	111.0	109.5	109.2	112.2
bc	109.8	108.4 (8)	108.9	108.4 (8)	108.7	108.4	110.2	108.5	109.8	107.8
bg	108.7		108.9		107.8	108.5	107.5	108.5	107.8	109.1
cg	108.7		109.8		107.8	107.9	107.5	109.3	107.8	107.9
de	109.8		108.9		108.7	108.4	112.8	112.0	112.8	111.7
df	108.7		108.9		107.8	108.5				
ef	108.7		109.8		107.8	107.9				
bad	58.9		-54.5		-117.0	-1.0	51.3	-69.5	-128.4	-19.7
bae	180.0		63.8		0.1	118.4	-173.2	61.2	4.5	113.8
baf	-60.5		-173.9		121.6	-120.4				
cad	180.0		63.8		0.1	118.4	173.2	50.5	-5.9	98.8
cae	-58.9		-178.0		117.2	-122.3	-51.3	-178.4	127.1	-127.7
caf	60.5		-55.7		-121.3	-1.0				
gad	-60.5		-173.9		121.6	-120.4	-67.7	170.0	112.8	-141.5
gae	60.5		-55.7		-121.3	-1.0	67.7	-59.3	-114.2	-8.0
gaf	180.0	180 (fixed)	66.6	67 (3)	0.1	120.2				

a) Electron diffraction data[23]

X = Cl (B3PW91 (LAV3P))

	CF_2ClCF_2Cl						CF_2ClCF_2•			
	A		G		T1	T2	A	G	T1	T2
	HF	Expt[b]	HF	Expt[b]	HF	HF	HF	HF	HF	HF
a	1.549	1.563 (7)	1.552	1.563 (7)	1.594	1.590	1.501	1.512	1.519	1.525
b	1.329	1.331 (2)	1.334	1.331 (2)	1.331	1.331	1.331	1.342	1.333	1.336
c	1.329		1.329		1.331	1.327	1.331	1.333	1.333	1.338
d	1.329		1.334		1.331	1.331	1.318	1.324	1.322	1.322
e	1.329		1.329		1.331	1.327	1.318	1.320	1.322	1.317
f	1.817	1.748 (3)	1.807	1.748 (3)	1.807	1.814				
g	1.817		1.807		1.807	1.814	1.856	1.818	1.834	1.822
ab	109.8	108.9 (3)	107.6	108.9 (3)	108.1	108.3	110.0	112.0	110.9	110.4
ac	109.8		109.8		108.1	111.6	110.0	109.0	111.0	109.6
ad	109.8		107.6		108.1	108.3	115.1	113.2	114.5	113.4
ae	109.8		109.8		108.1	111.6	115.1	115.1	114.5	117.8
af	109.5	110.7 (4)	111.6	110.7 (4)	115.5	111.4				
ag	109.5		111.6		115.5	111.4	111.2	109.7	109.6	111.9
bc	109.8	108.7 (3)	109.1	108.7 (3)	108.8	108.7	110.0	108.4	109.6	108.0
bg	108.9		108.9		108.1	108.5	107.8	108.4	107.9	109.0
cg	108.9		109.6		108.1	108.3	107.8	109.3	107.9	107.9
de	109.8		109.1		108.8	108.7	112.7	112.1	112.6	111.9
df	108.9		108.9		108.1	108.5				
ef	108.9		109.6		108.1	108.3				
bad	59.1		-55.4		-117.5	-1.0	52.5	-66.7	-127.7	-16.0
bae	180.0		63.3		0.0	118.6	-173.8	64.0	4.5	117.5
baf	-60.4		-174.8		121.3	-120.2				
cad	180.0		63.3		0.0	118.6	173.8	53.2	-5.6	102.8
cae	-59.1		-178.0		117.6	-121.8	-52.5	-176.0	126.5	-123.7
caf	60.4		-56.2		-121.2	-0.6				
gad	-60.4		-174.8		121.3	-120.2	-66.8	172.9	113.3	-137.6
gae	60.4		-56.2		-121.2	-0.6	66.8	-56.4	-114.5	-4.0
gaf	180.0	180 (fixed)	65.7	62.5 (13)	0.0	120.5				

b) Electron diffraction data[30]

Table S1d. The structural parameters of the CF_2XCF_2X and CF_2XCF_2• radicals (X = I, Br and Cl) optimized at B3PW91 (LAV3P(d)) level of theory. The bond length is given in angstrom and the angle is in degree. The prefix A-, G-, and T- mean anti-, gauche-, and transition state, respectively. *a* corresponds to the C-C bond, *b, c, d* and *e* correspond to C-F bonds, and *f* and *g* corresponds to C-X bonds.

X = I (B3PW91 (LAV3P(d))

	CF_2ICF_2I				CF_2ICF_2•			
	A	G	T1	T2	A	G	T1	T2
a	1.547	1.555	1.604	1.589	1.492	1.510	1.514	1.523
b	1.335	1.341	1.338	1.337	1.336	1.348	1.339	1.343
c	1.335	1.336	1.338	1.335	1.336	1.338	1.339	1.345
d	1.335	1.341	1.338	1.335	1.316	1.326	1.323	1.324
e	1.335	1.336	1.338	1.337	1.316	1.322	1.323	1.319
f	2.187	2.173	2.176	2.183				
g	2.187	2.173	2.176	2.183	2.233	2.180	2.198	2.185
ab	109.6	107.0	107.4	108.1	109.9	111.6	110.8	109.9
ac	109.6	109.4	107.4	111.3	109.8	108.5	110.8	109.0
ad	109.6	107.0	107.4	111.3	115.9	113.4	114.8	113.3
ae	109.6	109.4	107.4	108.1	115.9	115.2	114.8	118.3
af	110.6	113.0	118.3	112.8				
ag	110.6	113.0	118.3	112.8	111.5	110.1	109.5	112.9
bc	109.3	108.4	108.2	107.8	109.8	108.1	109.4	107.4
bg	108.8	110.0	107.6	108.8	107.8	109.0	108.2	109.3
cg	108.8	109.0	107.6	108.0	107.8	109.4	108.2	108.1
de	109.3	108.4	108.2	107.8	112.8	111.8	112.6	111.5
df	108.8	109.0	107.6	108.0				
ef	108.8	110.0	107.6	108.8				
bad	60.0	-52.0	-116.0	-1.5	51.8	-69.1	-127.5	-21.0
bae	180.0	65.2	0.2	116.7	-172.7	61.5	5.3	112.2
baf	-60.0	-171.9	112.1	-121.8				
cad	180.0	65.2	0.2	116.7	172.7	50.0	-6.0	96.4
cae	-60.0	-177.6	116.3	-125.1	-51.8	179.4	126.9	-130.3
caf	60.0	-54.7	-121.8	-3.6				
gad	-60.0	-171.9	122.1	-121.8	-67.8	169.7	113.3	-143.4
gae	60.0	-54.7	-121.8	-3.6	67.8	-59.7	-113.9	-10.1
gaf	180.0	68.2	0.2	118.0				

X = Br (B3PW91 (LAV3P(d))

	CF_2ICF_2I				CF_2ICF_2•			
	A	G	T1	T2	A	G	T1	T2
a	1.552	1.556	1.602	1.593	1.500	1.512	1.519	1.526
b	1.333	1.339	1.336	1.335	1.336	1.347	1.337	1.341
c	1.333	1.333	1.336	1.332	1.336	1.337	1.337	1.343
d	1.333	1.339	1.336	1.335	1.317	1.326	1.323	1.323
e	1.333	1.333	1.336	1.332	1.317	1.321	1.323	1.318
f	1.972	1.960	1.960	1.968				
g	1.972	1.960	1.960	1.968	2.006	1.967	1.983	1.971
ab	109.6	107.2	107.6	108.1	109.7	111.8	110.8	110.1
ac	109.6	109.5	107.7	111.4	109.7	108.7	110.8	109.2
ad	109.6	107.2	107.7	108.1	115.5	113.3	114.6	113.3
ae	109.6	109.5	107.7	111.4	115.5	115.1	114.6	118.2
af	110.1	112.3	116.7	112.0				
ag	110.1	112.3	116.7	112.0	111.6	109.9	109.4	112.4
bc	109.4	108.6	108.4	108.1	109.7	108.1	109.3	107.5
bg	109.0	109.1	108.1	108.8	108.1	108.8	108.3	109.3
cg	109.0	110.0	108.1	108.3	108.1	109.5	108.3	108.3
de	109.4	108.6	108.4	108.1	112.7	111.9	112.6	111.7
df	109.0	109.1	108.1	108.8				
ef	109.0	110.0	108.1	108.3				
bad	59.9	-54.2	-116.3	-0.4	52.6	-68.6	-127.4	-17.4
bae	180.0	63.5	0.3	118.2	-173.1	62.0	4.9	116.0
baf	-60.1	-174.1	112.0	-120.2				
cad	180.0	63.5	0.3	118.2	173.1	50.7	-5.9	100.4
cae	-59.9	178.9	116.9	-123.2	-52.6	-178.8	126.4	-126.2
caf	60.1	-56.4	-121.4	-1.6				
gad	-60.1	-174.1	122.0	-120.2	-67.2	170.5	113.3	-139.5
gae	60.1	-56.4	-121.4	-1.6	67.2	-58.9	-114.4	-6.1
gaf	180.0	66.1	0.3	119.9				

X = Cl (B3PW91 (LAV3P(d))

	CF_2ICF_2I				CF_2ICF_2•			
	A	G	T1	T2	A	G	T1	T2
a	1.555	1.557	1.601	1.597	1.508	1.515	1.526	1.529
b	1.335	1.339	1.337	1.336	1.338	1.349	1.339	1.341
c	1.335	1.335	1.336	1.333	1.338	1.339	1.339	1.345
d	1.335	1.339	1.336	1.336	1.319	1.324	1.323	1.322
e	1.335	1.335	1.337	1.334	1.319	1.322	1.323	1.319
f	1.768	1.762	1.762	1.766				
g	1.768	1.762	1.763	1.767	1.793	1.768	1.780	1.772
ab	109.2	107.4	107.8	108.0	109.1	111.3	110.2	109.7
ac	109.2	109.2	107.8	110.9	109.1	108.4	110.3	109.0
ad	109.2	107.4	107.8	108.0	114.9	113.2	114.3	113.8
ae	109.2	109.2	107.8	110.9	114.9	115.1	114.4	117.5
af	110.4	112.1	108.3	111.8				
ag	110.4	112.1	108.7	111.9	112.3	110.5	110.2	112.5
bc	109.2	108.6	108.2	108.1	109.4	107.8	108.9	107.5
bg	109.5	109.5	108.7	109.1	108.5	109.0	108.6	109.5
cg	109.5	110.1	108.7	108.8	108.5	109.8	108.5	108.5
de	109.2	108.6	108.3	108.1	112.4	112.0	112.3	111.8
df	109.5	109.5	108.7	109.1				
ef	109.5	110.1	108.7	108.8				
bad	60.7	-54.8	-116.7	1.2	54.0	-64.3	-126.4	-12.3
bae	180.0	62.7	0.0	119.5	-173.4	66.3	5.1	121.1
baf	-59.6	-175.1	121.7	-118.9				
cad	180.0	62.7	0.0	119.4	173.4	54.1	-6.0	105.1
cae	-60.7	-179.7	116.7	-122.3	-54.0	-175.3	125.4	-121.5
caf	59.6	-57.5	-121.7	-0.7				
gad	-59.6	-175.1	121.6	-118.9	-66.3	174.5	113.8	-134.5
gae	59.6	-57.5	-121.7	-0.7	66.3	-54.9	-114.7	-1.1
gaf	180.0	64.7	0.0	121.0				

Table S1e. The structural parameters of the CF_2XCF_2X and CF_2XCF_2• radicals (X = I, Br and Cl) optimized at B3PW91 (MSV) level of theory. The bond length is given in angstrom and the angle is in degree. The prefix A-, G-, and T- mean anti-, gauche-, and transition state, respectively. *a* corresponds to the C-C bond, *b, c, d* and *e* correspond to C-F bonds, and *f* and *g* corresponds to C-X bonds.

X = I (B3PW91 (MSV)

	CF_2ICF_2I				CF_2ICF_2•			
	A	G	T1	T2	A	G	T1	T2
a	1.529	1.538	1.582	1.566	1.486	1.491	1.497	1.500
b	1.394	1.396	1.394	1.393	1.394	1.410	1.397	1.402
c	1.394	1.394	1.394	1.395	1.394	1.395	1.397	1.405
d	1.394	1.396	1.394	1.393	1.363	1.367	1.366	1.365
e	1.394	1.394	1.394	1.395	1.363	1.367	1.366	1.365
f	2.167	2.167	2.174	2.173				
g	2.167	2.167	2.174	2.173	2.193	2.165	2.174	2.161
ab	108.4	107.1	107.5	108.2	108.4	111.1	110.3	109.5
ac	108.4	108.2	107.5	109.8	108.4	107.8	110.3	108.1
ad	108.4	107.1	107.5	108.2	116.1	115.9	116.4	115.7
ae	108.4	108.2	107.5	109.8	116.1	116.0	116.5	118.7
af	113.9	115.6	120.0	115.8				
ag	113.9	115.6	120.0	115.8	115.2	112.1	111.5	115.1
bc	107.5	107.0	106.7	106.0	108.4	106.5	108.0	105.9
bg	109.2	109.6	107.3	108.3	108.1	109.3	108.4	109.3
cg	109.2	109.0	107.3	108.3	108.1	109.8	108.3	108.5
de	107.5	107.0	106.7	106.0	111.9	111.6	112.5	111.2
df	109.2	109.0	107.3	108.3				
ef	109.2	109.6	107.3	108.3				
bad	63.6	-52.8	-114.4	-3.2	53.9	-67.9	-127.9	-18.9
bae	180.0	62.3	0.1	112.1	-171.4	65.9	8.6	117.3
baf	-58.2	-174.5	122.9	-125.0				
cad	180.0	62.3	0.1	112.1	171.4	48.5	-8.7	96.1
cae	-63.6	177.3	114.7	-132.6	-53.9	177.7	127.8	-127.8
caf	58.2	-59.4	-122.6	-9.7				
gad	-58.2	-174.5	122.9	-125.0	-67.3	169.4	111.7	-142.5
gae	58.2	-59.4	-122.6	-9.7	67.3	-56.8	-111.8	-6.3
gaf	180.0	63.8	0.2	113.3				

X = Br (B3PW91 (MSV)

	CF_2ICF_2I				CF_2ICF_2•			
	A	G	T1	T2	A	G	T1	T2
a	1.529	1.534	1.574	1.565	1.486	1.492	1.498	1.502
b	1.387	1.390	1.388	1.387	1.388	1.402	1.390	1.394
c	1.387	1.386	1.388	1.387	1.388	1.389	1.390	1.398
d	1.387	1.390	1.388	1.387	1.361	1.367	1.365	1.365
e	1.387	1.386	1.388	1.387	1.361	1.365	1.365	1.362
f	1.963	1.958	1.963	1.964				
g	1.963	1.958	1.963	1.964	2.001	1.964	1.985	1.967
ab	109.0	107.8	108.2	108.6	109.0	111.7	110.7	110.0
ac	109.0	109.0	108.2	110.6	109.0	108.4	110.7	108.7
ad	109.0	107.8	108.2	108.6	116.1	115.3	116.3	115.6
ae	109.0	109.0	108.2	110.6	116.1	116.2	116.3	118.8
af	112.5	113.7	117.5	114.1				
ag	112.5	113.7	117.5	114.1	113.9	111.3	110.9	114.0
bc	108.0	107.7	107.3	106.7	108.8	107.0	108.4	106.5
bg	109.1	109.0	107.7	108.4	108.0	108.8	108.0	109.3
cg	109.1	109.6	107.7	108.1	108.0	109.6	108.1	108.2
de	108.0	107.7	107.3	106.7	112.2	111.8	112.4	111.5
df	109.1	108.9	107.7	108.4				
ef	109.1	109.6	107.7	108.1				
bad	62.3	-53.0	-115.8	-0.2	53.2	-66.2	-128.0	-15.7
bae	180.0	63.6	0.1	116.6	-171.8	67.5	7.9	120.9
baf	-58.9	-173.8	122.2	-121.2				
cad	180.0	63.6	0.1	116.6	171.8	51.4	-7.8	100.5
cae	-62.3	-179.7	116.0	-126.6	-53.2	174.9	128.1	-122.9
caf	58.9	-57.2	-121.9	-4.4				
gad	-58.9	-173.8	122.2	-121.2	-67.5	172.1	112.1	-138.8
gae	58.9	-57.2	-121.9	-4.4	67.5	-54.2	-112.0	-2.2
gaf	180.0	65.4	0.1	117.8				

X = Cl (B3PW91 (MSV)

	CF_2ICF_2I				CF_2ICF_2•			
	A	G	T1	T2	A	G	T1	T2
a	1.533	1.537	1.573	1.568	1.486	1.494	1.498	1.503
b	1.379	1.384	1.382	1.381	1.382	1.396	1.384	1.389
c	1.379	1.379	1.382	1.378	1.382	1.383	1.385	1.391
d	1.379	1.384	1.382	1.381	1.360	1.367	1.364	1.364
e	1.379	1.379	1.382	1.378	1.360	1.363	1.363	1.360
f	1.846	1.838	1.840	1.845				
g	1.846	1.838	1.840	1.845	1.885	1.848	1.868	1.851
ab	109.7	108.5	108.7	108.9	110.0	112.5	111.4	110.8
ac	109.7	109.8	108.7	111.4	110.0	109.1	111.4	109.5
ad	109.7	108.5	108.7	108.9	116.0	115.0	116.2	115.2
ae	109.7	109.8	108.7	111.4	116.0	116.1	116.2	118.7
af	110.7	111.7	115.3	112.1				
ag	110.7	111.7	115.3	112.1	111.9	109.8	109.5	112.3
bc	108.7	108.2	107.9	107.5	109.2	107.5	108.8	106.9
bg	109.0	108.9	108.0	108.6	107.9	108.4	107.8	109.1
cg	109.0	109.7	108.0	108.2	107.9	109.4	107.8	108.0
de	108.7	108.2	107.9	107.5	112.5	112.0	112.7	111.8
df	109.0	108.9	108.0	108.6				
ef	109.0	109.7	108.0	108.2				
bad	60.6	-54.4	-117.3	-0.1	52.3	-68.2	-129.1	-16.3
bae	180.0	63.7	-0.1	118.4	-172.5	65.3	7.1	120.3
baf	-59.7	-174.5	121.3	-120.2				
cad	180.0	63.7	-0.1	118.4	172.5	51.0	-7.4	101.4
cae	-60.6	-178.3	117.1	-123.2	-52.23	175.5	128.8	-122.1
caf	59.7	-56.4	-121.5	-1.8				
gad	-59.7	-174.5	121.3	-120.2	-67.6	170.9	111.7	-138.6
gae	59.7	-56.4	-121.5	-1.8	67.6	-55.5	-112.1	-2.1
gaf	180.0	65.4	-0.1	119.6				

Table S1f. The structural parameters of the CF_2XCF_2X and CF_2XCF_2• radicals (X = I, Br and Cl) optimized at B3PW91 (MSV(d)) level of theory. The bond length is given in angstrom and the angle is in degree. The prefix A-, G-, and T- mean anti-, gauche-, and transition state, respectively. *a* corresponds to the C-C bond, *b, c, d* and *e* correspond to C-F bonds, and *f* and *g* corresponds to C-X bonds.

X = I (B3PW91 (MSV(d))

	CF_2ICF_2I				CF_2ICF_2•			
	A	G	T1	T2	A	G	T1	T2
a	1.542	1.552	1.601	1.586	1.490	1.506	1.511	1.520
b	1.336	1.343	1.339	1.338	1.337	1.350	1.340	1.345
c	1.336	1.337	1.339	1.337	1.337	1.339	1.340	1.346
d	1.336	1.343	1.339	1.338	1.318	1.327	1.324	1.325
e	1.336	1.337	1.339	1.337	1.318	1.324	1.324	1.321
f	2.198	2.186	2.189	2.193				
g	2.198	2.186	2.189	2.193	2.229	2.194	2.203	2.194
ab	109.5	106.7	107.4	108.0	110.2	111.5	111.0	110.1
ac	109.5	109.0	107.4	111.1	110.2	108.8	111.0	108.9
ad	109.5	106.7	107.4	108.0	115.3	113.9	114.9	113.4
ae	109.5	109.0	107.4	111.1	115.3	114.5	114.8	118.1
af	110.6	113.7	118.4	113.1				
ag	110.6	113.7	118.4	113.1	109.8	109.5	108.5	112.4
bc	109.3	108.5	108.2	107.8	109.8	108.3	109.3	107.3
bg	108.9	109.7	107.6	108.5	108.4	109.4	108.5	109.4
cg	108.9	109.1	107.6	108.1	108.4	109.3	108.5	108.5
de	109.3	108.5	108.2	107.8	112.7	112.0	112.8	111.6
df	108.9	109.1	107.6	108.5				
ef	108.9	109.7	107.6	108.1				
bad	60.1	-58.9	-116.6	-2.9	52.3	-75.2	-127.4	-23.6
bae	180.0	58.1	-0.5	115.2	-173.6	55.5	5.8	109.6
baf	-59.9	-179.2	121.4	-123.1				
cad	180.0	58.1	-0.5	115.2	173.6	44.2	-5.6	93.8
cae	-60.1	175.1	115.6	-126.7	-52.3	174.9	127.6	-132.9
caf	59.9	-62.2	-122.5	-5.0				
gad	-59.9	-179.2	121.4	-123.1	-67.0	163.5	113.5	-145.9
gae	59.9	-62.2	-122.5	-5.0	67.0	-65.7	-113.3	-12.6
gaf	180.0	60.5	-0.5	116.8				

X = Br (B3PW91 (MSV(d))

	CF_2ICF_2I				CF_2ICF_2•			
	A	G	T1	T2	A	G	T1	T2
a	1.544	1.549	1.594	1.587	1.497	1.508	1.516	1.521
b	1.335	1.341	1.337	1.336	1.337	1.349	1.339	1.343
c	1.335	1.335	1.337	1.334	1.337	1.339	1.339	1.345
d	1.335	1.341	1.337	1.336	1.319	1.323	1.324	1.324
e	1.335	1.335	1.337	1.334	1.319	1.323	1.324	1.319
f	1.948	1.936	1.938	1.944				
g	1.948	1.936	1.938	1.944	1.982	1.944	1.958	1.948
ab	109.5	107.4	107.8	108.2	109.6	111.6	110.7	110.1
ac	109.5	109.4	107.8	111.3	109.6	108.7	110.7	109.1
ad	109.5	107.4	107.8	108.2	115.2	113.4	114.6	113.5
ae	109.5	109.4	107.8	111.3	115.2	114.9	114.6	118.1
af	110.0	111.8	116.2	112.0				
ag	110.0	111.8	116.2	112.0	111.3	109.8	109.3	112.3
bc	109.3	108.6	108.3	107.9	109.6	108.2	109.2	107.5
bg	109.2	109.3	108.2	108.9	108.3	109.0	108.4	109.3
cg	109.2	110.1	108.2	108.4	108.3	109.6	108.4	108.4
de	109.3	108.6	108.3	107.9	112.7	112.0	112.5	111.8
df	109.2	109.3	108.2	108.9				
ef	109.2	110.1	108.2	108.4				
bad	60.1	-56.5	-116.8	-0.1	52.8	-69.6	-126.7	-17.9
bae	180.0	61.3	-0.1	118.4	-173.2	61.1	5.5	115.8
baf	-60.0	-176.4	121.6	-120.1				
cad	180.0	61.3	-0.1	118.4	173.2	49.6	-5.4	99.8
cae	-60.0	179.1	116.6	-123.2	-52.8	179.8	126.8	-126.5
caf	60.0	-58.6	-121.7	-1.6				
gad	-60.0	-176.4	121.6	-120.1	-67.0	169.5	113.9	-139.9
gae	60.0	-58.6	-121.7	-1.6	67.0	-59.9	-113.9	-6.3
gaf	180.0	63.6	-0.1	119.9				

X = Cl (B3PW91 (MSV(d))

	CF_2ICF_2I				CF_2ICF_2•			
	A	G	T1	T2	A	G	T1	T2
a	1.551	1.553	1.597	1.592	1.504	1.511	1.523	1.525
b	1.336	1.340	1.338	1.337	1.339	1.350	1.340	1.343
c	1.336	1.336	1.337	1.334	1.339	1.340	1.340	1.346
d	1.336	1.340	1.338	1.337	1.320	1.326	1.324	1.324
e	1.336	1.336	1.337	1.335	1.320	1.322	1.324	1.319
f	1.770	1.763	1.763	1.768				
g	1.770	1.763	1.764	1.768	1.795	1.770	1.781	1.773
ab	109.2	107.5	107.9	108.1	109.1	111.2	110.3	109.9
ac	109.2	109.2	107.9	110.9	109.1	108.5	110.3	108.9
ad	109.2	107.5	107.9	108.1	114.9	113.2	114.4	113.8
ae	109.2	109.2	107.9	110.9	114.9	115.0	114.4	117.5
af	110.3	111.8	115.1	111.7				
ag	110.3	111.8	115.1	111.7	112.2	110.4	110.1	112.3
bc	109.1	108.6	108.2	108.0	109.4	107.9	108.9	107.4
bg	109.5	109.5	108.8	109.2	108.5	109.0	108.6	109.6
cg	109.5	110.2	108.8	108.8	108.5	109.9	108.6	108.6
de	109.1	108.6	108.2	108.1	112.5	112.1	112.4	111.9
df	109.5	109.5	108.8	109.2				
ef	109.5	110.2	108.8	108.8				
bad	60.8	-55.8	-116.7	1.3	53.8	-65.2	-126.3	-13.1
bae	180.0	61.8	0.1	119.6	-173.3	65.4	5.5	120.5
baf	-59.6	-176.0	121.7	-118.8				
cad	180.0	61.8	0.0	119.5	173.3	53.3	-5.9	104.4
cae	-60.8	179.4	116.8	-122.2	-53.8	176.1	125.9	-122.1
caf	59.6	-58.4	-121.6	-0.6				
gad	-59.6	-176.0	121.7	-118.9	-66.4	173.7	113.9	-135.3
gae	59.6	-58.4	-121.6	-0.6	66.4	-55.7	-114.4	-1.8
gaf	180.0	63.7	0.0	121.0				

Table S2. The total energies calculated at various levels of theory for CF_2XCF_2X and CF_2XCF_2• radicals (X = I, Br, Cl). Zero point energies are given in the parenthesis. The energies are in hartrees and the difference energies, zero point energies and experimental values are in kcal/mol.

CF_2XCF_2X

Method	A-CF_2ICF_2I	G-CF_2ICF_2I	T1-CF_2ICF_2I	T2-CF_2ICF_2I
HF (LAV3P)	-495.75091 (15.31)	-495.74518 (15.30)	-495.72891 (15.18)	-495.73732 (15.27)
HF (LAV3P(d))	-495.76559	-495.76084	-495.74470	-495.75257
LMP2//HF (LAV3P)	-496.73633	-496.73285	-496.71765	-496.72439
LMP2//HF (LAV3P(d))	-496.89951	-496.89646	-496.88199	-496.88871
B3PW91 (LAV3P)	-498.17647 (14.39)	-498.17208 (14.80)	-498.15940 (14.27)	-498.16599 (14.33)
B3PW91 (LAV3P(d))	-498.18764	-498.18330	-498.17171	-498.17796
B3PW91 (MSV)	-14304.37211	-14304.36686	-14304.35343	-14304.36102
B3PW91 (MSV(d))	-14304.64320	-14304.63910	-14304.62672	-14304.63321
Method	A-CF_2BrCF_2Br	G-CF_2BrCF_2Br	T1-CF_2BrCF_2Br	T2-CF_2BrCF_2Br
HF (LAV3P)	-499.29963 (15.85)	-499.29599 (15.83)	-499.28135 (15.82)	-499.28713 (15.65)
HF (LAV3P(d))	-499.32776	-499.32531	-499.31096	-499.31575
LMP2//HF (LAV3P)	-500.29297	-500.29125	-500.27828	-500.28222
LMP2//HF (LAV3P(d))	-500.48345	-500.48175	-500.46927	-500.47330
B3PW91 (LAV3P)	-501.73728 (14.85)	-501.73464 (14.81)	-501.72339 (14.76)	-501.72787 (14.82)
B3PW91 (LAV3P(d))	-501.75803	-501.75618	-501.74559	-501.74948
B3PW91 (MSV)	-5617.83150	-5617.82859	-5617.81691	-5617.82200
B3PW91 (MSV(d))	-5618.15262	-5618.15069	-5618.13973	-5618.14354
Method	A-CF_2ClCF_2Cl	G-CF_2ClCF_2Cl	T1-CF_2ClCF_2Cl	T2-CF_2ClCF_2Cl
HF (LAV3P)	-502.86834 (16.80)	-502.86640 (16.83)	-502.85346 (16.80)	-502.85688 (16.81)
HF (LAV3P(d))	-502.90520	-502.90392	-502.89080	-502.89377
LMP2//HF (LAV3P)	-503.87189	-503.87115	-503.86011	-503.86252
LMP2//HF (LAV3P(d))	-504.09539	-504.09473	-504.08308	-504.08554
B3PW91 (LAV3P)	-505.30851 (15.71)	-505.30714 (15.67)	-505.29724 (15.68)	-505.72787 (15.69)
B3PW91 (LAV3P(d))	-505.33587	-505.33521	-505.32551	-505.32785
B3PW91 (MSV)	-1393.97389	-1393.97238	-1393.96173	-1393.96503
B3PW91 (MSV(d))	-1394.13947	-1394.13897	-1394.12936	-1394.13142

CF_2XCF_2• radicals

Method	A-CF_2ICF_2	G-CF_2ICF_2	T1-CF_2ICF_2	T2-CF_2ICF_2	B-CF_2ICF_2
HF (LAV3P)	-484.56037 (14.20)	-484.55579 (14.16)	-484.55149 (14.07)	-484.55183 (14.09)	-484.46074 (13.37)
HF (LAV3P(d))	-484.56793	-484.56370	-484.55945	-484.55957	-484.47216
LMP2//HF (LAV3P)	-485.48135	-485.47563	-485.47160	-485.47241	-485.41942
LMP2//HF (LAV3P(d))	-485.57701	-485.57164	-485.56789	-485.56896	-485.51973
B3PW91 (LAV3P)	-486.71635 (13.27)	-486.70835 (13.27)	-486.70551 (13.00)	-486.70640 (13.13)	-486.65886 (12.31)
B3PW91 (LAV3P(d))	-486.72154	-486.71418	-486.71133	-486.71224	-486.66830
B3PW91 (MSV)	-7389.50604	-7389.50133	-7389.49810	-7389.49970	-7389.45262
B3PW91 (MSV(d))	-7389.70407	-7389.69648	-7389.69357	-7389.69461	-7389.65182
Method	A-CF_2BrCF_2	G-CF_2BrCF_2	T1-CF_2BrCF_2	T2-CF_2BrCF_2	B-CF_2BrCF_2
HF (LAV3P)	-486.33507 (14.45)	-486.33114 (14.42)	-486.32705 (14.33)	-486.32697 (14.37)	-486.21793 (13.68)
HF (LAV3P(d))	-486.34914	-486.34579	-486.34161	-486.34131	-486.23280
LMP2//HF (LAV3P)	-487.25946	-487.25479	-487.25093	-487.25117	-487.18413
LMP2//HF (LAV3P(d))	-487.36917	-487.36474	-487.36122	-487.36159	-487.29700
B3PW91 (LAV3P)	-488.49597 (13.50)	-488.48955 (13.41)	-488.48681 (13.26)	-488.48723 (13.37)	-488.42624(13.06)
B3PW91 (LAV3P(d))	-488.50548	-488.50020	-488.49726	-488.49783	-488.43807
B3PW91 (MSV)	-3046.23564	-3046.23161	-3046.22812	-3046.22940	-3046.16589
B3PW91 (MSV(d))	-3046.45685	-3046.45178	-3046.44854	-3046.44938	-3046.38745
Method	A-CF_2ClCF_2	G-CF_2ClCF_2	T1-CF_2ClCF_2	T2-CF_2ClCF_2	B-CF_2ClCF_2
HF (LAV3P)	-488.11909 (14.93)	-488.11616 (14.90)	-488.11187 (14.81)	-488.11188 (14.83)	-487.97955 (13.42)
HF (LAV3P(d))	-488.13714	-488.13466	-488.13004	-488.13016	-488.09235
LMP2//HF (LAV3P)	-489.04824	-489.04489	-489.04068	-489.04114	-488.94788
LMP2//HF (LAV3P(d))	-489.17387	-489.17097	-489.16693	-489.16759	-489.11880
B3PW91 (LAV3P)	-490.27995 (13.90)	-490.27556 (13.84)	-490.27235 (13.73)	-490.27301 (13.79)	-490.25819 (13.58)
B3PW91 (LAV3P(d))	-490.29261	-490.28925	-490.28559	-490.28658	-490.25986
B3PW91 (MSV)	-934.30735	-934.30364	-934.30045	-934.30110	-934.28597
B3PW91 (MSV(d))	-934.44897	-934.44572	-934.44205	-934.44303	-934.41767

Halogen atoms and $CF_2=CF_2$

Method	I	Br	Cl	$CF_2=CF_2$
HF (LAV3P)	-11.15723	-12.91863	-14.68120	-473.41578 (14.13)
HF (LAV3P(d))	-11.15723	-12.91863	-14.68120	-473.41578
LMP2//HF (LAV3P)	-11.17128	-12.93869	-14.70823	-474.31729
LMP2//HF (LAV3P(d))	-11.24707	-13.02050	-14.79872	-474.31729
B3PW91 (LAV3P)	-11.38531	-13.15084	-14.91530	-475.32740 (13.20)
B3PW91 (LAV3P(d))	-11.38531	-13.15084	-14.91530	-475.32740
B3PW91 (MSV)	-6914.78155	-2571.49856	-459.56382	-474.71385
B3PW91 (MSV(d))	-6914.85751	-2571.58622	-459.56382	-474.83278

Table S3. Total energy (hartree) of CH_2XCH_2X calculated at various levels of theory. The zero point energies (kcal/mol) are also presented in the parenthesis.

Method	A-CH_2ClCH_2Cl	G-CH_2ClCH_2Cl	T1-CH_2ClCH_2Cl	T2-CH_2ClCH_2Cl
HF (LAV3P)	-107.48309	-107.47967	-107.46583	-107.47488
	(36.71)	(36.71)	(36.68)	(36.61)
LMP2//HF (LAV3P)	-107.84102	-107.83872	-107.82677	-107.83283
LMP2 (LAV3P)	-107.84155	-107.83917	-107.82709	-107.83332
	(36.70)	(36.63)	(36.55)	(36.43)
B3PW91 (LAV3P)	-108.53653	-108.53386	-108.52146	-108.52900
	(35.60)	(35.53)	(35.49)	(35.38)
B3LYP (LAV3P)	-108.52082	-108.51794	-108.50562	-108.51333
	(35.48)	(35.41)	(35.36)	(35.25)

Method	A-CH_2BrCH_2Br	G-CH_2BrCH_2Br	T1-CH_2BrCH_2Br	T2-CH_2BrCH_2Br
HF (LAV3P)	-103.92640	-103.92161	-103.90824	-103.91738
	(35.89)	(35.85)	(35.79)	(35.80)
LMP2//HF (LAV3P)	-104.27160	-104.26830	-104.25643	-104.26246
LMP2 (LAV3P)	-104.27218	-104.26877	-104.25679	-104.26303
	(35.89)	(35.81)	(35.68)	(35.64)
B3PW91 (LAV3P)	-104.97538	-104.97124	-104.95956	-104.96683
	(34.80)	(34.75)	(34.67)	(34.62)
B3LYP (LAV3P)	-104.95736	-104.95290	-104.94133	-104.94891
	(34.68)	(34.61)	(34.54)	(34.50)

Method	A-CH_2ICH2I	G-CH_2ICH_2I	T1-CH_2ICH_2I	T2-CH_2ICH_2I
HF (LAV3P)	-100.38301	-100.37718	-100.36450	-100.37339
	(35.38)	(35.32)	(35.24)	(35.32)
LMP2//HF (LAV3P)	-100.71969	-100.71558	-100.70376	-100.71011
LMP2 (LAV3P)	-100.72028	-100.71602	-100.70416	-100.71070
	(35.42)	(35.34)	(35.17)	(35.19)
B3PW91 (LAV3P)	-101.42044	-101.41519	-101.40448	-101.41086
	(34.33)	(34.26)	(34.17)	(34.18)
B3LYP (LAV3P)	-101.39825	-101.39259	-101.38195	-101.38883
	(34.22)	(34.20)	(34.05)	(34.07)

Table S4. Relative energies (kcal/mol) of CH_2XCH_2X calculated at various levels of theory.

Method	A-CH_2ClCH_2Cl	G-CH_2ClCH_2Cl	T1-CH_2ClCH_2Cl	T2-CH_2ClCH_2Cl
HF	-2.15	0	8.65	2.90
LMP2//HF	-1.44	0	7.47	3.60
LMP2	-1.42	0	7.50	3.47
B3PW91	-1.61	0	7.74	2.90
B3LYP	-1.74	0	7.68	2.73
experiment	-1.0 ~ -1.5	0		

Method	A-CH_2BrCH_2Br	G-CH_2BrCH_2Br	T1-CH_2BrCH_2Br	T2-CH_2BrCH_2Br
HF	-2.97	0	8.33	2.61
LMP2//HF	-2.03	0	7.39	3.62
LMP2	-2.06	0	7.39	3.43
B3PW91	-2.55	0	7.25	2.64
B3LYP	-2.71	0	7.19	2.39
experiment	-1.4 ~ -2.2	0		

Method	A-CH_2ICH_2I	G-CH_2ICH_2I	T1-CH_2ICH_2I	T2-CH_2ICH_2I
HF	-3.60	0	7.88	2.38
LMP2//HF	-2.52	0	7.34	3.44
LMP2	-2.60	0	7.27	3.19
B3PW91	-3.22	0	6.63	2.64
B3LYP	-3.54	0	6.52	2.23
experiment	-1.38 ~ -2.6	0		

Table S5. Vibrational frequencies and mode analysis for CF_2XCF_2X parent molecules (B3PW91 (LAV3P))

a. Anti conformer

Freq(cm-1)		CF_2ClCF_2Cl	Freq(cm^{-1})		CF_2BrCF_2Br	Freq(cm^{-1})		CF_2ICF_2I
1330	A_g	C-C str	1308	A_g	C-C str	1280	A_g	C-C str
1292	A_u	C-F str asym	1286	A_u	C-F str asym	1263	A_u	C-F str asym
1277	B_g	C-F str asym	1274	B_g	C-F str asym	1255	B_g	C-F str asym
1189	B_u	C-F str sym, F-C-F scissor	1185	B_u	F-C-F scissor	1174	B_u	C-F str sym, F-C-F scissor
1039	A_g	C-Cl str	998	A_g	C-Br str sym	985	A_g	C-I str
802	B_u	C-Cl str	727	B_u	C-Br str	693	B_u	C-I str
707	A_g	C-F str sym Cl-C-C bend	694	A_g	Br-C-C bend sym	684	A_g	C-F str sym F-C-F scissor, I-C-C bend
604	B_u	F-C-F scissor	589	B_u	C-F str sym	578	B_u	F-C-F scissor
536	B_g	twist	521	B_g	twist	517	B_g	twist
415	B_u	C-Cl str	361	A_g	C-F str sym	360	A_g	F-C-C bend
408	A_g	wag, C-Cl str	317	B_u	C-Br str	287	A_u	twist
370	A_u	twist	308	A_u	twist	276	B_u	C-I str
358	A_g	F-C-C bend	296	A_g	wag, C-Br str	262	B_g	rock
318	B_g	rock	280	B_g	Rock	261	A_g	wag
249	A_g	Cl-C-C bend	207	A_u	F-C-C bend	205	A_u	F-C-C bend
213	A_u	F-C-C bend	170	A_g	C-Br str Br-C-C bend	130	A_g	C-I str
165	B_u	Cl-C-C bend	126	B_u	Br-C-C bend	109	B_u	I-C-C bend
68	A_u	torsion	62	A_u	torsion	57	A_u	torsion

b. gauche conformer

Freq(cm^{-1})		CF_2ClCF_2Cl	Freq(cm^{-1})		CF_2BrCF_2Br	Freq(cm^{-1})		CF_2ICF_2I
1323	A	C-C str	1295	A	C-C str	1260	A	C-C str
1273	B	C-F str asym	1263	B	C-F str asym	1242	B	C-F str asym
1264	A	C-F str asym	1254	A	C-F str asym	1234	A	C-F str asym
1164	B	C-F str sym F-C-F scissor	1151	B	C-F str sym F-C-F scissor	1135	B	C-F str sym F-C-F scissor
1036	A	C-Cl str F-C-F scissor	1008	A	C-Br str F-C-F scissor	994	A	C-I str F-C-F scissor
883	B	C-Cl str	842	B	C-Br str	821	B	C-I str
670	A	C-F str sym	650	A	C-F str sym	640	A	C-F str sym
618	B	F-C-F scissor	601	B	F-C-F scissor	587	B	F-C-F scissor
482	A	twist F-C-C bend	456	A	twist, F-C-C bend	447	A	twist, F-C-C bend
422	B	rock, C-Cl str	354	B	twist, Br-C-C bend F-C-C bend	333	B	twist, I-C-C bend F-C-C bend
418	A	rock, C-Cl str	320	A	F-C-C bend	305	A	F-C-C bend
393	B	twist, Cl-C-C bend F-C-C bend	309	B	rock	276	B	rock
323	A	F-C-C bend	302	A	rock	276	A	rock
305	A	F-C-C bend	271	A	Br-C-F bend	245	A	I-C-F bend
303	B	rock	259	B	F-C-C bend	231	B	F-C-C bend
195	B	F-C-C bend	173	B	rock, F-C-C bend	156	B	rock, I-C-C bend
165	A	Cl-C-C bend	113	A	Br-C-C bend	93	A	I-C-C bend
62	A	torsion	58	A	torsion	55	A	torsion

c. Rotational transition state T1

Freq(cm^{-1})		CF_2ClCF_2Cl	Freq(cm^{-1})		CF_2BrCF_2Br	Freq(cm^{-1})		CF_2ICF_2I
1271	A	C-C str C-F str asym	1261	B	C-F str asym	1241	B	C-F str asym
1270	B	C-F str asym	1250	A	C-F str asym	1231	A	C-F str asym
1262	A	C-F str sym	1243	A	C-C str, C-F str sym	1213	A	C-C str, C-F str sym
1164	B	C-F str sym	1149	B	C-F str sym	1134	B	C-F str sym
991	A	C-C str C-Cl str	947	A	C-C str C-Br str	919	A	C-C str C-I str
900	B	C-Cl str	861	B	C-Br str	841	B	C-I str
634	A	C-Cl str, F-C-F scissor	603	B	F-C-F scissor	589	B	F-C-F scissor
624	B	F-C-F scissor Cl-C-C bend	600	A	F-C-F scissor	586	A	F-C-F scissor
525	A	twist	504	A	twist	491	A	twist
424	A	C-Cl str	370	A	wag	369	A	wag
416	B	C-Cl str, rock	338	B	F-C-C bend	333	B	F-C-C bend
378	B	rock	311	B	rock, C-Br str	275	B	rock
363	A	wag	310	A	C-Br str	266	B	rock
310	A	rock	282	B	rock	264	A	C-I str
298	B	F-C-C bend	273	A	rock	256	A	rock
274	B	Cl-C-C bend	213	B	Br-C-C bend	181	B	I-C-C bend
200	A	Cl-C-C bend	128	A	Br-C-C bend	103	A	I-C-C bend
66*i*	A	torsion	53*i*	A	torsion	53*i*	A	torsion

d. Rotational transition state T2

Freq(cm^{-1})		CF_2ClCF_2Cl	Freq(cm^{-1})		CF_2BrCF_2Br	Freq(cm^{-1})		CF_2ICF_2I
1281	A	C-C str C-F str asym	1270	A	C-F str asym	1248	A	C-F str asym
1276	A	C-C str, C-F str asym	1266	B	C-F str asym	1243	B	C-F str asym
1274	B	C-F str sym	1256	A	C-C str, C-Br str	1228	A	C-C str, C-I str
1176	B	C-F str sym	1170	B	C-F str sym, C-Br str	1158	B	C-F str sym, C-I str
1021	A	C-C str C-Cl str	988	A	C-C str C-F str sym	971	A	C-C str C-F str sym
824	B	C-Cl str, wag	768	B	C-Br str, F-C-C bend	742	B	C-I str, F-C-C bend
694	A	F-C-F scissor	678	A	F-C-F scissor	669	A	F-C-F scissor
623	B	F-C-F scissor	608	B	F-C-F scissor	598	B	F-C-F scissor
475	B	rock	437	B	rock	422	B	rock
418	A	rock	396	A	wag	394	A	wag
414	B	rock	331	A	F-C-C bend	325	A	F-C-C bend
407	A	twist	318	B	rock	283	A	rock
356	A	wag	310	A	rock	282	B	rock
317	B	F-C-C bend	287	A	twist	250	A	twist
312	B	F-C-C bend	273	B	F-C-C bend	245	B	F-C-C bend
227	A	Cl-C-C bend	175	B	Br-C-C bend	150	B	I-C-C bend
223	B	Cl-C-C bend	157	A	Br-C-C bend	124	A	I-C-C bend
61*i*	A	torsion	51*i*	A	torsion	44*i*	A	torsion

Table S6. Vibrational frequencies and mode analysis for CF_2XCF_2 radicals (B3PW91 (LAV3P))

a. Anti conformer

Freq(cm^{-1})		CF_2ClCF_2	Freq(cm^{-1})		CF_2BrCF_2	Freq(cm^{-1})		CF_2ICF_2
1243	A'	C-C str	1230	A'	C-C str	1246	A'	C-C str
1355	A"	C-F str asym (rad)	1365	A"	C-F str asym (rad)	1366	A"	C-F str (rad)
1277	A"	C-F str asym (Cl)	1276	A"	C-F str asym (Br)	1261	A"	C-F str (I)
1188	A'	C-F str sym	1186	A'	C-F str sym	1178	A'	C-F str sym
889	A'	C-F str sym	845	A'	C-F str sym	822	A'	C-F str sym, C-C str
676	A'	wag, C-Cl str	660	A'	wag, C-Br str	647	A'	wag, C-I str
623	A'	wag, C-Cl str	588	A'	F-C-F scissor	575	A'	F-C-F scissor
567	A'	F-C-F scissor	552	A'	wag, C-Br str	541	A'	wag, C-I str
519	A"	twist	512	A"	twist	511	A"	twist
377	A'	C-Cl str	366	A'	F-C-C bend	365	A'	F-C-C bend
364	A'	F-C-C bend	287	A"	rock	265	A"	rock
331	A"	rock	269	A'	C-Br str	225	A'	C-I str
200	A"	F-C-C bend	199	A"	F-C-C bend	198	A"	F-C-C bend
162	A'	Cl-C-C bend	130	A'	Br-C-C bend	115	A'	I-C-C bend
70	A"	torsion	70	A"	torsion	72	A"	torsion

b. Gauche conformer

Freq(cm^{-1})	CF_2ClCF_2	Freq(cm^{-1})	CF_2BrCF_2	Freq(cm^{-1})	CF_2ICF_2
1394	C-C str	1383	C-C str	1368	C-C str
1331	C-F str asym (rad)	1326	C-F str asym (rad)	1319	C-F str asym (rad)
1238	C-F str asym (Cl)	1234	C-F str asym (Br)	1216	C-F str asym (I)
1138	C-F str sym	1131	C-F str sym	1117	C-F str sym
955	C-Cl str	922	C-Br str, C-F str sym	911	C-F str sym
772	wag, C-Cl str	764	wag, C-Br str	761	C-I str wag, C-I str
627	wag, C-Cl str	613	wag, C-Br str	608	wag, C-I str
578	F-C-F scissor	571	F-C-F scissor	564	F-C-F scissor
448	twist	438	twist	434	twist
410	C-Cl str	307	F-C-C bend	294	F-C-C bend
340	rock	295	rock	267	rock
317	F-C-C bend	288	C-Br str, rock	249	C-I str
210	F-C-C bend	208	F-C-C bend	206	F-C-C bend
176	Cl-C-C bend, F-C-C bend	148	Br-C-C bend	133	I-C-C bend
46	torsion	44	torsion	42	torsion

c. Rotational transition state T1

Freq(cm^{-1})	CF_2ClCF_2	Freq(cm^{-1})	CF_2BrCF_2	Freq(cm^{-1})	CF_2ICF_2
1391	C-C str	1387	C-C str	1374	C-C str
1339	C-F str asym (rad)	1340	C-F str asym (rad)	1336	C-F str asym (rad)
1264	C-F str asym (Cl)	1262	C-F str asym (Br)	1245	C-F str asym (I)
1153	C-F str sym	1145	C-F str sym	1132	C-F str sym
904	C-Cl str, C-F str sym	868	C-Br str, C-F str sym	851	C-I str, C-F str sym
753	wag, C-Cl str	734	wag, C-Br str	725	wag, C-I str
576	F-C-F scissor	565	F-C-F scissor	558	F-C-F scissor
508	wag, C-Cl str	495	twist	490	twist
504	twist	474	wag, C-Br str	461	wag, C-I str
403	C-Cl str	310	F-C-C bend sym	302	F-C-C bend sym
330	rock	292	C-Br str	265	rock
325	F-C-C bend sym	288	rock	248	C-I str
246	F-C-C bend asym	243	F-C-C bend asym	242	F-C-C bend asym
201	Cl-C-C bend	161	Br-C-C bend	139	I-C-C bend
60*i*	torsion	53*i*	torsion	58*i*	torsion

d. Rotational transition state T2

Freq(cm^{-1})	CF_2ClCF_2	Freq(cm^{-1})	CF_2BrCF_2	Freq(cm^{-1})	CF_2ICF_2
1388	C-C str	1380	C-C str	1367	C-C str
1339	C-F str asym (rad)	1334	C-F str asym (rad)	1328	C-F str asym (rad)
1225	C-F str asym (Cl)	1216	C-F str asym (Br)	1196	C-F str asym (I)
1159	C-F str sym	1152	C-F str sym	1140	C-F str sym
945	C-Cl str, C-F str sym	920	C-Br str, C-F str sym	910	C-I str, C-F str sym
700	wag, C-Cl str	687	wag, C-Br str	681	wag, C-I str
632	F-C-F scissor sym	625	F-C-F scissor sym	622	F-C-F scissor sym
583	F-C-F scissor asym	579	F-C-F scissor asym	576	F-C-F scissor asym
414	C-Cl str	390	twist	391	twist
390	F-C-C bend	357	F-C-C bend	342	rock
389	twist	303	C-Br str	273	F-C-C bend
320	rock	274	rock	255	wag, F-C-C bend
259	wag, F-C-C bend	257	wag, F-C-C bend	239	C-I str
207	Cl-C-C bend	169	Br-C-C bend	149	I-C-C bend
64*i*	torsion	61*i*	torsion	61*i*	torsion

Table S7. Vibrational frequencies and mode analysis for CF_2XCF_2X parent molecules (HF (LAV3P))

a. Anti conformer

Freq(cm-1)		CF_2ClCF_2Cl	Freq(cm^{-1})		CF_2BrCF_2Br	Freq(cm^{-1})		CF_2ICF_2I
1492	A_g	C-C str	1460	A_g	C-C str	1420	A_g	C-C str
1422	A_u	C-F str asym	1410	A_u	C-F str asym	1377	A_u	C-F str asym
1414	B_g	C-F str asym	1402	B_g	C-F str asym	1372	B_g	C-F str asym
1298	B_u	C-F str sym, F-C-F scissor	1287	B_u	F-C-F scissor	1272	B_u	C-F str sym, F-C-F scissor
1163	A_g	C-Cl str	1127	A_g	C-Br str sym	1119	A_g	C-I str
895	B_u	C-Cl str	811	B_u	C-Br str	776	B_u	C-I str
763	A_g	C-F str sym Cl-C-C bend	748	A_g	Br-C-C bend sym	735	A_g	C-F str sym F-C-F scissor, I-C-C bend
652	B_u	F-C-F scissor	634	B_u	C-F str sym	621	B_u	F-C-F scissor
588	B_g	twist	571	B_g	twist	567	B_g	twist
459	B_u	C-Cl str	392	A_g	C-F str sym	392	A_g	F-C-C bend
459	A_g	wag, C-Cl str	353	B_u	C-Br str	316	A_u	twist
405	A_u	twist	340	A_u	twist	307	B_u	C-I str
391	A_g	F-C-C bend	330	A_g	wag, C-Br str	291	A_g	wag
351	B_g	rock	311	B_g	rock	288	B_g	rock
270	A_g	Cl-C-C bend	229	A_u	F-C-C bend	226	A_u	F-C-C bend
230	A_u	F-C-C bend	190	A_g	C-Br str Br-C-C bend	146	A_g	C-I str
179	B_u	Cl-C-C bend	134	B_u	Br-C-C bend	112	B_u	I-C-C bend
68	A_u	torsion	69	A_u	torsion	55	A_u	torsion

b. Gauche conformer

Freq(cm^{-1})		CF_2ClCF_2Cl	Freq(cm^{-1})		CF_2BrCF_2Br	Freq(cm^{-1})		CF_2ICF_2I
1486	A	C-C str	1448	A	C-C str	1405	A	C-C str
1407	B	C-F str asym	1389	B	C-F str asym	1360	B	C-F str asym
1402	A	C-F str asym	1385	A	C-F str asym	1356	A	C-F str asym
1279	B	C-F str sym F-C-F scissor	1257	B	C-F str sym F-C-F scissor	1239	B	C-F str sym F-C-F scissor
1164	A	C-Cl str F-C-F scissor	1128	A	C-Br str F-C-F scissor	1119	A	C-I str F-C-F scissor
981	B	C-Cl str	930	B	C-Br str	911	B	C-I str
728	A	C-F str sym	704	A	C-F str sym	691	A	C-F str sym
671	B	F-C-F scissor	650	B	F-C-F scissor	633	B	F-C-F scissor
534	A	twist F-C-C bend	501	A	twist, F-C-C bend	490	A	twist, F-C-C bend
470	B	rock, C-Cl str	387	B	twist, Br-C-C bend F-C-C bend	364	B	twist, I-C-C bend F-C-C bend
463	A	rock, C-Cl str	356	A	F-C-C bend, C-Br str	338	A	F-C-C bend
432	B	twist, Cl-C-C bend F-C-C bend	342	B	rock	306	B	rock
356	A	F-C-C bend	329	A	F-C-C bend	301	A	rock
341	B	F-C-C bend	306	A	Br-C-F bend	274	A	I-C-F bend
340	A	Cl-C-F bend	292	B	F-C-C bend	261	B	F-C-C bend
215	B	F-C-C bend	189	B	F-C-C bend, Br-C-C bend	170	B	rock, I-C-C bend
182	A	Cl-C-C bend	125	A	Br-C-C bend	102	A	I-C-C bend
76	A	torsion	64	A	torsion	62	A	torsion

c. Rotational transition state T1

Freq(cm^{-1})		CF_2ClCF_2Cl	Freq(cm^{-1})		CF_2BrCF_2Br	Freq(cm^{-1})		CF_2ICF_2I
1427	A	C-C str C-F str asym	1389	A	C-C str	1355	A	C-C str
1400	B	C-F str asym	1384	B	C-F str asym	1355	B	C-F str asym
1399	A	C-F str sym	1383	A	C-F str sym	1347	A	C-F str sym
1278	B	C-F str sym	1252	B	C-F str sym	1232	B	C-F str sym
1114	A	C-C str C-Cl str	1064	A	C-Br str, C-C str	1040	A	C-I str, C-C str
995	B	C-Cl str	949	B	C-Br str	929	B	C-I str
688	A	C-Cl str, F-C-F scissor	651	B	F-C-F scissor	634	B	F-C-F scissor
675	B	F-C-F scissor Cl-C-C bend	649	A	F-C-F scissor	634	A	F-C-F scissor
580	A	twist	556	A	twist	543	A	twist
468	A	C-Cl str	402	A	wag	399	A	wag
464	B	C-Cl str, rock	372	B	F-C-C bend	366	B	F-C-C bend
420	B	rock	344	B	rock, C-Br str	301	B	rock
397	A	wag	343	A	C-Br str	292	A	C-I str
347	A	rock	302	B	rock	283	B	rock
323	B	F-C-C bend	302	A	rock	277	A	rock
307	B	Cl-C-C bend	237	B	Br-C-C bend	203	B	I-C-C bend
218	A	Cl-C-C bend	138	A	Br-C-C bend	102	A	I-C-C bend
76*i*	A	torsion	72*i*	A	torsion	77*i*	A	torsion

d. Rotational transition state T2

Freq(cm^{-1})		CF_2ClCF_2Cl	Freq(cm^{-1})		CF_2BrCF_2Br	Freq(cm^{-1})		CF_2ICF_2I
1433	A	C-C str	1402	A	C-C str	1370	A	C-C str
1407	A	C-F str asym,	1390	A	C-F str asym	1359	A	C-F str asym
1407	B	C-F str asym	1390	B	C-F str asym	1353	B	C-C str,
1269	B	C-F str sym	1275	B	C-F str sym, C-Br str	1260	B	C-F str sym, C-I str
1154	A	C-C str C-Cl str	1118	A	C-C str C-F str sym	1107	A	C-C str C-F str sym
919	B	C-Cl str, wag	855	B	C-Br str, F-C-C bend	829	B	C-I str, F-C-C bend
751	A	F-C-F scissor	732	A	F-C-F scissor	721	A	F-C-F scissor
673	B	F-C-F scissor	657	B	F-C-F scissor	644	B	F-C-F scissor
524	B	rock	478	B	rock	461	B	rock
468	A	rock	433	A	wag	431	A	wag
458	B	rock	364	A	F-C-C bend	355	A	F-C-C bend
448	A	twist	352	B	rock	311	B	rock
391	A	wag	339	A	twist	308	A	twist
351	B	F-C-C bend	318	A	rock	276	A	rock
348	B	F-C-C bend	303	B	F-C-C bend	273	B	F-C-C bend
249	A	Cl-C-C bend	193	B	Br-C-C bend	165	B	I-C-C bend
245	B	Cl-C-C bend	172	A	Br-C-C bend	137	A	I-C-C bend
-68*i*	A	torsion	57*i*	A	torsion	48*i*	A	torsion

Table S8. Vibrational frequencies and mode analysis for CF_2XCF_2 radicals (HF (LAV3P))

a. Anti conformer

Freq(cm^{-1})		CF_2ClCF_2	Freq(cm^{-1})		CF_2BrCF_2	Freq(cm^{-1})		CF_2ICF_2
1545	A'	C-C str	1532	A'	C-C str	1515	A'	C-C str
1457	A"	C-F str asym (rad)	1457	A"	C-F str asym (rad)	1451	A"	C-F str (rad)
1408	A"	C-F str asym (Cl)	1395	A"	C-F str asym (Br)	1370	A"	C-F str (I)
1294	A'	C-F str sym	1286	A'	C-F str sym	1274	A'	C-F str sym
1080	A'	wag, C-Cl str	1050	A'	wag, C-Br str	1043	A'	wag, C-I str
739	A'	C-F str sym	730	A'	C-F str sym	722	A'	C-F str sym
715	A'	wag, C-Cl str	664	A'	wag, C-Br str	642	A'	wag, C-Br str
618	A'	F-C-F scissor	610	A'	F-C-F scissor	605	A'	F-C-F scissor
565	A"	twist	555	A"	twist	552	A"	twist
443	A'	C-Cl str	393	A'	F-C-C bend	390	A'	F-C-C bend
391	A'	F-C-C bend	327	A"	rock	295	A"	rock
368	A"	rock	319	A'	C-Br str	282	A'	C-I str
220	A"	F-C-C bend	217	A"	F-C-C bend	218	A"	F-C-C bend
192	A'	Cl-C-C bend	149	A'	Br-C-C bend	138	A'	I-C-C bend
75	A"	torsion	70	A"	torsion	74	A"	torsion

b. Gauche conformer

Freq(cm^{-1})	CF_2ClCF_2	Freq(cm^{-1})	CF_2BrCF_2	Freq(cm^{-1})	CF_2ICF_2
1536	C-C str	1520	C-C str	1502	C-C str
1441	C-F str asym (rad)	1436	C-F str asym (rad)	1429	C-F str asym (rad)
1381	C-F str asym (Cl)	1370	C-F str asym (Br)	1345	C-F str asym (I)
1274	C-F str sym	1262	C-F str sym	1248	C-F str sym
1078	C-Cl str C-F str sym	1044	C-Br str, C-F str sym	1037	C-F str sym C-I str
887	wag, C-Cl str	876	wag, C-Br str	872	wag, C-I str
691	F-C-F scissor	676	F-C-F scissor	670	F-C-F scissor
627	F-C-F scissor	619	F-C-F scissor	612	F-C-F scissor
494	twist	477	twist	473	twist
456	C-Cl str	340	F-C-C bend	322	F-C-C bend
377	rock	325	rock	295	rock
346	F-C-C bend	319	C-Br str, rock	279	C-I str
241	F-C-C bend	240	F-C-C bend	239	F-C-C bend
194	Cl-C-C bend, F-C-C bend	163	Br-C-C bend	147	I-C-C bend
64	torsion	62	torsion	62	torsion

c. Rotational transition state T1

Freq(cm^{-1})	CF_2ClCF_2	Freq(cm^{-1})	CF_2BrCF_2	Freq(cm^{-1})	CF_2ICF_2
1525	C-C str	1514	C-C str	1497	C-C str
1446	C-F str asym (rad)	1444	C-F str asym (rad)	1440	C-F str asym (rad)
1403	C-F str asym (Cl)	1392	C-F str asym (Br)	1367	C-F str asym (I)
1276	C-F str sym	1254	C-F str sym	1250	C-F str sym
1024	C-Cl str, C-F str sym	984	C-Br str, C-F str sym	972	C-I str, C-F str sym
876	wag, C-Cl str	869	wag, C-Br str	865	wag, C-I str
628	F-C-F scissor	618	F-C-F scissor	610	F-C-F scissor
616	F-C-F scissor	593	F-C-F scissor	586	F-C-F scissor
555	twist	542	twist	537	twist
453	C-Cl str	347	wag	342	wag
366	rock	332	C-Br str	295	rock
356	F-C-C bend sym	318	rock	286	C-I str
266	F-C-C bend asym	263	F-C-C bend asym	260	F-C-C bend asym
227	Cl-C-C bend	183	Br-C-C bend	161	I-C-C bend
67*i*	torsion	65*i*	torsion	65*i*	torsion

d. Rotational transition state T2

Freq(cm^{-1})	CF_2ClCF_2	Freq(cm^{-1})	CF_2BrCF_2	Freq(cm^{-1})	CF_2ICF_2
1516	C-C str	1503	C-C str	1485	C-C str
1448	C-F str asym (rad)	1445	C-F str asym (rad)	1436	C-F str asym (rad)
1374	C-F str asym (Cl)	1360	C-F str asym (Br)	1334	C-F str asym (I)
1281	C-F str sym	1271	C-F str sym	1257	C-F str sym
1083	C-Cl str, C-F str sym	1053	C-Br str, C-F str sym	1044	C-I str, C-F str sym
780	wag, C-Cl str	759	wag, C-Br str	751	wag, C-I str
720	F-C-F scissor sym	711	F-C-F scissor sym	705	F-C-F scissor sym
635	F-C-F scissor asym	629	F-C-F scissor asym	624	F-C-F scissor asym
470	C-Cl str	421	twist	420	twist
436	F-C-C bend	410	F-C-C bend	396	rock
420	twist	339	C-Br str	309	F-C-C bend
357	rock	311	rock	287	wag, F-C-C bend
288	wag, F-C-C bend	293	wag, F-C-C bend	271	C-I str
231	Cl-C-C bend	188	Br-C-C bend	166	I-C-C bend
69*i*	torsion	67*i*	torsion	67*i*	torsion

Table S9. MSV(d) basis set for C, F, Cl, Br, and I.

Atom	Function	Exponent	Coefficient
C	S	426.100000000000	2.097797009752951E-02
		64.2200000000000	0.142886782983173
		14.3200000000000	0.479230978943563
		3.78400000000000	0.500827619941020
	S	5.02000000000000	-0.195941725088570
		0.528500000000000	1.07271908501021
	S	0.163200000000000	1.00000000000000
	P	9.55800000000000	5.637939631776828E-02
		2.02100000000000	0.311876407098290
		0.550000000000000	0.761900208240117
	P	0.152400000000000	1.00000000000000
	D	0.800000000000000	1.00000000000000
F	S	992.800000000000	2.049937459807006E-02
		149.500000000000	0.141169621986709
		33.4800000000000	0.479134790954891
		8.96300000000000	0.500751942952856
	S	12.6700000000000	-0.194997008079080
		1.37600000000000	1.07425918492655
	S	0.406300000000000	1.00000000000000
	P	22.6700000000000	6.486085724363115E-02
		4.98400000000000	0.340386062228974
		1.34900000000000	0.734731037494245
	P	0.347700000000000	1.00000000000000
	D	0.800000000000000	1.00000000000000

Cl	S	3644.00000000000	2.020008079827341E-02
		549.300000000000	0.139814876988049
		123.700000000000	0.480948279958891
		33.5100000000000	0.498428707957397
	S	47.9800000000000	-0.110538798010178
		6.68100000000000	0.475462701043779
		2.43600000000000	0.610153027056181
	S	4.40300000000000	-0.312627131952709
		0.561300000000000	1.12043444624658
	S	0.196100000000000	1.00000000000000
	P	133.900000000000	3.395905409223948E-02
		30.7700000000000	0.203104193953585
		9.12300000000000	0.518451969881520
		2.89400000000000	0.436301064900294
	P	1.76700000000000	8.502592820462777E-02
		0.701500000000000	0.932834217050772
	P	0.196000000000000	1.00000000000000
	D	0.750000000000000	1.00000000000000

Br	S	15690.0000000000	2.005409390159184E-02
		2366.00000000000	0.139148767011045
		534.600000000000	0.483172871038353
		145.800000000000	0.495763820039352
	S	209.000000000000	-0.129402412033746
		36.4100000000000	0.437059346113978
		14.2700000000000	0.655277576170886
	S	21.9700000000000	-0.261951703832504
		4.72000000000000	0.476204836695508
		1.87200000000000	0.677155797567016
	S	2.61000000000000	-0.558403306892908
		0.415300000000000	1.20759135544325
	S	0.153100000000000	1.00000000000000
	P	733.400000000000	2.932212709920819E-02
		171.900000000000	0.189532181994882
		53.2100000000000	0.521445373985919
		18.3000000000000	0.429631047988398
	P	12.3000000000000	6.465841919522045E-02
		6.19900000000000	0.510100782962293
		2.15900000000000	0.519376689961608
	P	4.95800000000000	-7.274844476209696E-02
		0.517000000000000	1.01656167505982
	P	0.153800000000000	1.00000000000000
	D	65.3100000000000	7.369196417280957E-02
		18.2500000000000	0.364265144865596
		5.97700000000000	0.714869328736232
	D	1.91500000000000	1.00000000000000
	D	0.338000000000000	1.00000000000000

I	S	36220.0000000000	1.996342370082851E-02
		5461.00000000000	0.138714698005757
		1235.00000000000	0.483557477020068
		337.400000000000	0.495477801020563
	S	482.000000000000	-0.135193513988191
		92.1400000000000	0.407543355964401
		36.3300000000000	0.688051319939898
	S	52.0200000000000	-0.336253055192589
		16.6000000000000	0.342699923196281
		6.84500000000000	0.859161714492084
	S	8.81800000000000	-0.471446175039328
		3.12300000000000	0.484940710040453
		1.24400000000000	0.808677575067459
	S	1.52600000000000	-0.756445126797422
		0.318800000000000	1.31909915313437
	S	0.123800000000000	1.00000000000000
	P	1808.00000000000	2.819335490447407E-02
		425.600000000000	0.186557030029605
		133.300000000000	0.523205440083029
		46.7800000000000	0.426506076067683
	P	28.9900000000000	6.684416238993790E-02
		19.0000000000000	0.490127391926221
		7.67100000000000	0.511428958923014
	P	14.3300000000000	-3.500068521310603E-02
		3.20100000000000	0.575302814215423
		1.25800000000000	0.502370060188113
	P	1.77900000000000	-2.152339671826118E-02
		0.348300000000000	1.00996065616450
	P	0.112800000000000	1.00000000000000
	D	231.200000000000	4.065184528411743E-02
		67.3300000000000	0.230875547909798
		23.8200000000000	0.532546493791935
		8.83100000000000	0.404395711842004
	D	8.14000000000000	0.217929100943697
		3.23900000000000	0.835574883784124
	D	1.14300000000000	1.00000000000000
	D	0.26600000000000	1.00000000000000