Supporting Information

Density Functional and Ab Initio Investigation of CF_2ICF_2I and CF_2CF_2I radical in Gas and Solution Phases

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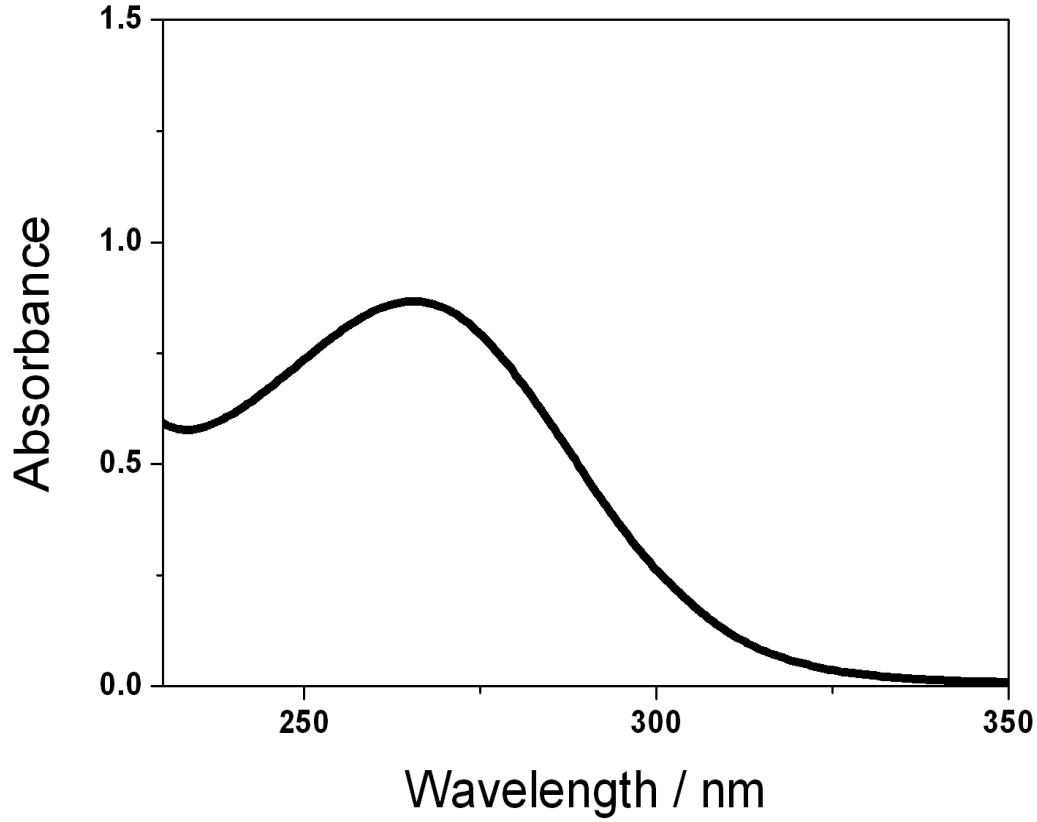

Figure S1. UV/VIS absorption spectra of CF_2ICF_2I in methanol. Methyl alcohol for the solvent was received from CARLO ERBA whose quality was over 99.9% purity. 1,2-diiodotetrafluoroethane (96%, stab. with copper) was purchased from Alfa Aesar and diluted with methanol to 0.68 mM solution. A 10-mm path length quartz SUPRASIL cell from Hellma was used for sample holding. We recorded the absorption spectrum from 190 nm to 600 nm at room temperature with a UV-Vis spectrophotometer (UV-2550, SHIMADU). A peak corresponding to n → σ* transition is observed at 265.5 nm.

Table S1. Optimized geometries (bond lengths in Å and bond angles in degrees) of CF_2ICF_2I and relative energies between anti and gauche structures in the gas phase.[a]

CF_2ICF_2I /Gas	Geom.	HF	MP2	CAS(12,12)	CASPT2	B3LYP	B3PW91	PBE0	X3LYP	M05-2X	[c]Exp.
Anti (C_{2h}, ^1A_g)	**C-C**	1.542	1.542	1.534	1.538	1.551	1.549	1.545	1.550	1.532	1.534±0.013
	C-F	1.313	1.340	1.312	1.343	1.340	1.334	1.331	1.339	1.335	1.328±0.003
	C-I	2.158	2.131	2.210	2.146	2.191	2.176	2.166	2.188	2.152	2.136±0.007
	∠CCF	109.28	109.16	109.75	109.15	109.58	109.65	109.61	109.56	109.34	109.4±1.0
	∠FCF	108.43	108.45	108.85	108.49	108.57	108.75	108.77	108.57	108.80	107.8±1.0
	∠CCI	112.03	110.93	111.58	111.01	111.44	110.92	110.77	111.41	110.65	111.6±1.0
Gauche **(C_2, ^1A)**	**C-C**	1.550	1.549	1.540	1.546	1.562	1.559	1.555	1.560	1.541	1.534±0.013
	C-F	1.314	1.340	1.312	1.343	1.341	1.335	1.331	1.339	1.336	1.328±0.003
	C-F′	1.318	1.345	1.316	1.347	1.346	1.340	1.337	1.345	1.341	
	C-I	2.148	2.124	2.202	2.140	2.179	2.164	2.154	2.175	2.143	2.136±0.007
	∠CCF	108.98	108.94	109.55	108.94	109.22	109.30	109.27	109.20	109.02	109.4±1.0
	∠CCF′	107.00	107.27	107.59	107.29	107.41	107.50	107.42	107.38	107.29	
	∠FCF	107.71	107.76	108.16	107.83	107.77	107.93	107.98	107.78	108.02	107.8±1.0
	∠CCI	114.53	112.83	114.09	113.27	113.76	113.09	112.97	113.75	113.02	111.6±1.0
	∠ICCI	67.03	65.48	67.20	66.91	67.36	66.36	66.39	67.44	66.96	70±3
[b]$\Delta E_{gauche\text{-}anti}$ (kcal/mol)		2.47 (2.44)	1.19 (1.15)	2.12 (2.09)	2.35	2.27 (2.23)	1.95 (1.92)	1.94 (1.90)	2.29 (2.25)	1.92 (1.79)	1.835±0.1[d] 1.22±0.36[e] 1.10-1.27[f]

[a]The molecular structure is depicted in Figure 1.
[b]Values in parenthesis are zero point energy corrected relative energies.
[c]Reference[1]
[d]Reference[2]
[e]Reference[3]
[f]$\Delta H°$ values, reference[4]

Table S2. Optimized geometries (bond lengths in Å and bond angles in degrees) of CF_2ICF_2I and relative energies between anti and gauche structures in methanol.[a]

CF_2ICF_2I /Methanol	Geom.	HF	MP2	CAS(12,12)	CASPT2	B3LYP	B3PW91	PBE0	X3LYP	M05-2X
Anti (C_{2h}, ^1A_g)	**C-C**	1.542	1.541	1.534	1.538	1.552	1.549	1.545	1.550	1.532
	C-F	1.316	1.344	1.313	1.344	1.344	1.337	1.334	1.342	1.339
	C-I	2.155	2.127	2.209	2.145	2.187	2.172	2.162	2.183	2.148
	∠CCF	109.06	108.89	109.67	109.04	109.34	109.43	109.39	109.30	109.07
	∠FCF	108.15	108.14	108.75	108.43	108.24	108.48	108.51	108.25	108.48
	∠CCI	112.39	111.37	111.68	111.11	111.83	111.30	111.14	111.85	111.17
***Gauche* (C_2, ^1A)**	**C-C**	1.549	1.548	1.540	1.546	1.561	1.558	1.554	1.560	1.540
	C-F	1.317	1.344	1.313	1.345	1.345	1.338	1.334	1.343	1.339
	C-F′	1.322	1.349	1.318	1.349	1.351	1.344	1.340	1.349	1.345
	C-I	2.145	2.119	2.200	2.137	2.173	2.159	2.150	2.170	2.138
	∠CCF	108.71	108.68	109.48	108.82	108.93	109.06	109.05	108.93	108.74
	∠CCF′	106.85	107.12	107.61	107.28	107.26	107.41	107.33	107.23	107.13
	∠FCF	107.37	107.37	108.07	107.63	107.39	107.62	107.66	107.39	107.65
	∠CCI	114.80	113.14	114.09	113.35	114.08	113.32	113.21	114.06	113.33
	∠ICCI	66.64	65.29	67.18	66.87	66.96	66.15	66.20	67.25	66.72
[b]$\Delta E_{gauche\text{-}anti}$ (kcal/mol)		2.31 (2.26)	1.08	2.03	2.25	2.13 (2.08)	1.86 (1.80)	1.85 (1.80)	2.14 (2.08)	1.77 (1.59)

[a]The molecular structure is depicted in Figure 1.
[b]Values in parenthesis are zero point energy corrected relative energies.

Table S3. Vibrational frequencies (cm^{-1}) of CF_2ICF_2I in the gas phase and methanol (in parenthesis).

CF_2ICF_2I			HF	MP2	CAS(12,12)	B3LYP	B3PW91	PBE0	X3LYP	M05-2X	Exp.
Anti (C_{2h})	A_u	torsion	57(57)	55	59	46(48)	48(50)	49(51)	46(48)	61(61)	
	B_u	CCI bend	112(111)	107	108	101(101)	102(102)	103(103)	101(101)	111(110)	
	A_g	CCI bend	146(146)	140	132	129(130)	132(132)	134(135)	130(131)	143(142)	133[a]
	A_u	CF_2 twist	236(233)	218	236	216(214)	215(214)	215(214)	216(215)	225(223)	
	B_g	CF_2 twist	286(285)	264	274	255(255)	258(258)	260(260)	255(256)	271(271)	
	A_g	C-I stretch	298(298)	283	272	263(264)	269(270)	274(275)	265(266)	287(288)	268[a]
	B_u	C-I stretch	317(317)	305	284	280(282)	287(289)	294(295)	282(285)	308(308)	
	A_u	CF_2 twist	316(314)	293	300	282(281)	285(285)	288(287)	283(282)	299(298)	
	A_g	CF_2 scissor	397(395)	365	398	360(358)	362(361)	366(365)	361(360)	372(371)	
	B_g	CF_2 rock	571(570)	524	566	514(513)	517(517)	523(522)	516(515)	534(533)	
	B_u	CF_2 scissor	636(631)	577	632	574(569)	580(576)	585(581)	576(571)	587(582)	575[a],581[b]
	A_g	CF_2 scissor	745(742)	680	736	674(671)	681(679)	689(686)	677(674)	699(695)	670[a]
	B_u	CF_2 wag	787(767)	737	734	694(673)	705(684)	717(696)	698(678)	748(728)	709[a],709[b]
	A_g	C-C stretch	1110(1101)	1021	1102	959(949)	972(962)	991(981)	965(956)	1029(1019)	995-997[a]
	B_u	symm C-F stretch	1256(1224)	1139	1258	1115(1083)	1135(1104)	1153(1123)	1121(1090)	1171(1139)	1108[a],1116[b]
	B_g	asymm C-F stretch	1335(1304)	1174	1351	1150(1116)	1178(1146)	1200(1170)	1157(1124)	1217(1185)	
	A_u	asymm C-F stretch	1335(1292)	1189	1348	1158(1110)	1187(1143)	1211(1167)	1165(1120)	1230(1184)	1159[a],1169[b]
	A_g	C-C stretch + symm C-F stretch	1385(1371)	1264	1405	1214(1199)	1237(1223)	1260(1246)	1222(1206)	1297(1284)	
***Gauche* (C_2)**	A	torsion	58(59)	58	59	49(50)	51(52)	52(53)	49(50)	56(46)	
	A	CF_2 rock + CCI bend	99(99)	95	97	90(90)	90(91)	91(91)	90(90)	99(91)	
	B	CCF bend + CCI bend	172(171)	162	165	155(155)	156(156)	158(158)	156(156)	168(167)	
	B	CF_2 twist + C-I stretch	269(270)	249	246	238(239)	241(242)	244(245)	239(241)	250(251)	
	A	CF_2 twist + C-I stretch	278(279)	258	254	247(248)	250(251)	253(254)	248(249)	261(263)	
	B	FCI bend	308(308)	292	287	275(276)	280(281)	284(285)	276(277)	292(291)	

A	FCI bend	309(309)	296	290	277(278)	284(284)	289(289)	279(279)	297(296)	
A	CF_2 wag	334(332)	308	327	301(301)	301(301)	303(303)	302(302)	310(310)	
B	FCI bend	364(361)	338	351	329(328)	331(330)	334(333)	331(329))	342(338)	
A	FCI bend	495(495)	457	488	445(444)	449(449)	454(454)	447(446)	463(462)	
B	CF_2 scissor	646(639)	586	641	583(577)	589(583)	594(588)	585(579)	596(586)	
A	CF_2 scissor	706(701)	645	697	638(633)	645(641)	652(649)	640(635)	660(651)	
B	CF_2 wag	930(917)	860	907	831(817)	841(828)	852(839)	835(822)	866(853)	835[a],841[b]
A	C-C stretch	1103(1085)	1016	1077	963(944)	979(960)	998(979)	969(951)	1028(1008)	974[a],982[b]
B	symm C-F stretch	1226(1198)	1103	1234	1077(1042)	1094(1064)	1113(1085)	1080(1049)	1128(1100)	
A	asymm C-F stretch	1315(1279)	1162	1332	1130(1091)	1158(1121)	1181(1146)	1138(1099)	1198(1161)	
B	asymm C-F stretch	1318(1275)	1175	1333	1143(1098)	1170(1127)	1193(1152)	1150(1105)	1210(1167)	
A	C-C stretch + symm C-F stretch	1366(1345)	1246	1391	1191(1169)	1216(1194)	1239(1219)	1199(1176)	1275(1256)	1207[a],1215[b]

[a]Reference[5]
[b]Reference[4]

Table S4. The vertical excitation energies (T_v in eV) and oscillator strengths (in parenthesis, × 10^{-3}) of CF_2ICF_2I at the CASPT2 optimized geometry in the gas phase.

CF_2ICF_2I	State	B3LYP	M05-2X
	^3B_u	3.67	4.03
	^3A_u	3.70	4.06
	^3B_g	3.80	4.12
Anti	^3A_g	3.90	4.21
(C_{2h})	^1B_u	4.23(9.6)	4.68(6.3)
	^1A_u	4.28	4.73
	^1B_g	4.40	4.81
	^1A_g	4.52	4.88

Table S5. Optimized geometries (bond lengths in Å and bond angles in degrees) of •CF_2CF_2I radical and relative energies in the gas phase.[a]

•CF_2CF_2I /Gas	Geom.	HF	MP2	CAS(7,7)	CASPT2	B3LYP	B3PW91	PBE0	X3LYP	M05-2X	[c]Exp.
Anti (C_S, $^2A'$)	C-C	1.506	1.507	1.503	1.500	1.493	1.492	1.492	1.493	1.489	1.478±0.049
	C-F	1.313	1.341	1.313	1.343	1.340	1.335	1.331	1.339	1.335	1.340±0.037
	C-F′	1.295	1.317	1.297	1.320	1.316	1.311	1.308	1.315	1.312	1.277±0.027
	C-I	2.175	2.140	2.220	2.167	2.237	2.217	2.201	2.232	2.182	2.153±0.013
	∠CCF	109.11	108.96	109.32	109.28	110.11	110.09	110.00	110.08	109.78	108.6±6.0
	∠CCF′	114.92	114.53	114.77	114.70	116.38	116.34	116.04	116.29	115.46	117.9±3.1
	∠FCF	108.63	108.71	108.89	108.91	109.19	109.30	109.29	109.18	109.29	108.0±11.2
	∠F′CF′	111.77	111.91	111.70	112.06	112.30	112.43	112.41	112.29	112.40	119.8±7.8
	∠CCI	112.47	111.61	112.32	111.13	111.66	111.31	111.14	111.62	111.04	115.0±3.1
Gauche (C_1, ^2A)	C-C	1.515	1.513	1.511	1.510	1.512	1.509	1.508	1.511	1.502	
	$C-F_1$	1.321	1.352	1.319	1.354	1.356	1.350	1.345	1.355	1.348	
	$C-F_2$	1.315	1.342	1.314	1.344	1.343	1.337	1.333	1.341	1.338	
	$C-F_3$	1.300	1.322	1.302	1.325	1.326	1.321	1.317	1.324	1.319	
	$C-F_4$	1.298	1.320	1.299	1.323	1.322	1.317	1.313	1.320	1.316	
	C-I	2.148	2.124	2.200	2.140	2.179	2.166	2.156	2.176	2.145	
	$\angle CCF_1$	110.10	110.18	110.72	110.39	111.25	111.50	111.30	111.16	110.65	-
	$\angle CCF_2$	108.36	108.41	108.83	108.48	108.72	108.77	108.74	108.71	108.68	
	$\angle CCF_3$	113.30	113.27	113.17	113.57	114.41	114.48	115.46	114.33	113.83	
	$\angle CCF_4$	114.62	114.44	114.33	114.33	115.54	115.63	114.23	115.48	115.03	
	$\angle F_1CF_2$	107.72	107.53	108.21	107.69	107.47	107.61	107.64	107.47	107.67	
	$\angle F_3CF_4$	111.12	111.28	111.07	111.45	111.39	111.52	111.53	111.39	111.66	
	∠CCI	111.62	110.68	111.00	110.51	110.60	110.02	110.03	110.64	110.31	
$\Delta E_{gauche\text{-anti}}$ (kcal/mol)		2.61 (2.61)	2.52 (2.36)	2.31 (2.30)	2.91	3.85 (3.77)	3.70 (3.62)	3.62 (3.55)	3.82 (3.75)	3.30 (3.26)	-
Bridge (C_{2V}, $^2B_2$)	C-C	-	1.527	1.524	1.535	1.540	1.538	1.534	1.538	1.519	-
	C-F		1.333	1.301	1.330	1.329	1.324	1.321	1.328	1.323	

C-I		2.237	2.556	2.403	2.433	2.400	2.384	2.429	2.403
∠CCF		115.99	115.01	115.16	115.37	115.48	115.48	115.36	115.32
∠FCF		109.75	110.63	110.50	110.15	110.24	110.32	110.18	110.82
∠CCI		70.05	72.65	71.38	71.55	71.31	71.24	71.54	71.57
[b]$\Delta E_{bridge\text{-}anti}$ (kcal/mol)	-	42.49 (41.34)	42.71 (41.63)	32.71	31.78 (30.86)	31.31 (30.40)	32.34 (31.41)	32.23 (31.31)	36.89 (35.84)	-

[a]The molecular structure is depicted in Figure 1.
[b]Values in parenthesis are zero point energy corrected relative energies.
[c]Reference[6]

Table S6. Optimized geometries (bond lengths in Å and bond angles in degrees) of $\bullet CF_2CF_2I$ radical and relative energies in methanol.[a]

$\bullet CF_2CF_2I$ /Methanol	Geom.	HF	MP2	CAS(7,7)	CASPT2	B3LYP	B3PW91	PBE0	X3LYP	M05-2X
Anti (C_S, $^2A'$)	C-C	1.506	1.507	1.503	1.500	1.492	1.492	1.492	1.492	1.489
	C-F	1.315	1.344	1.314	1.343	1.342	1.336	1.332	1.341	1.337
	C-F′	1.297	1.318	1.298	1.320	1.317	1.312	1.309	1.315	1.313
	C-I	2.173	2.138	2.223	2.168	2.238	2.219	2.202	2.232	2.181
	∠CCF	109.04	108.84	109.51	109.37	110.14	110.14	110.03	110.09	109.78
	∠CCF′	114.73	114.35	114.59	114.56	116.24	116.20	115.89	116.13	115.30
	∠FCF	108.47	108.42	108.91	108.84	109.03	109.15	109.17	109.01	109.14
	∠F′CF′	111.61	111.85	111.59	112.04	112.36	112.50	112.45	112.34	112.42
	∠CCI	112.65	111.83	112.20	111.18	111.87	111.48	111.29	111.83	111.18
Gauche (C_1, ^2A)	C-C	1.515	1.513	1.511		1.510	1.508	1.507	1.509	1.501
	$C-F_1$	1.326	1.356	1.321		1.362	1.354	1.349	1.360	1.353
	$C-F_2$	1.318	1.345	1.315		1.347	1.340	1.337	1.345	1.341
	$C-F_3$	1.302	1.324	1.303		1.327	1.322	1.318	1.326	1.320
	$C-F_4$	1.299	1.320	1.300		1.322	1.317	1.314	1.321	1.317
	C-I	2.143	2.119	2.199		2.173	2.161	2.151	2.170	2.140
	$\angle CCF_1$	109.82	109.94	110.80	-	111.07	111.43	111.22	110.98	110.44
	$\angle CCF_2$	108.23	108.20	108.86		108.49	108.63	108.56	108.48	108.50
	$\angle CCF_3$	113.34	113.32	113.22		114.54	114.70	114.37	114.44	113.89
	$\angle CCF_4$	114.53	114.45	114.25		115.61	115.59	115.46	115.55	115.03
	$\angle F_1CF_2$	107.30	107.09	108.04		106.99	107.27	107.27	106.99	107.21
	$\angle F_3CF_4$	110.97	111.16	111.01		111.32	111.52	111.49	111.32	111.57
	∠CCI	111.96	111.08	110.98		111.01	110.26	110.29	111.05	110.73
$\Delta E_{gauche\text{-}anti}$ (kcal/mol)		2.38 (2.36)	2.38	2.24	-	3.60 (3.53)	3.52 (3.49)	3.45 (3.37)	3.57 (3.50)	3.11 (3.06)
Bridge (C_{2V}, $^2B_2$)	C-C	-	1.525	1.523	1.534	1.536	1.534	1.531	1.534	1.517
	C-F		1.335	1.302	1.331	1.332	1.327	1.323	1.331	1.325

C-I		2.233	2.559	2.399	2.422	2.394	2.379	2.421	2.400
∠CCF		115.97	115.04	115.22	115.45	115.56	115.54	115.42	115.37
∠FCF		109.54	110.61	110.46	109.95	110.13	110.22	110.01	110.72
∠CCI		70.03	72.69	71.36	71.51	71.31	71.24	71.53	71.58
[b]$\Delta E_{bridge\text{-}anti}$ (kcal/mol)	-	43.14	42.49	32.47	31.53 (30.63)	31.13 (30.28)	32.14 (31.22)	31.97 (31.06)	36.64 (35.57)

[a]The molecular structure is depicted in Figure 1.
[b]Values in parenthesis are zero point energy corrected relative energies.

Table S7. Vibrational frequencies (cm^{-1}) of $•CF_2CF_2I$ in the gas phase and (methanol).

$•CF_2CF_2I$			HF	MP2	CAS(7,7)	B3LYP	B3PW91	PBE0	X3LYP	M05-2X
Anti (C_S)	A"	torsion	83(83)	77	82	75(76)	76(65)	75(79)	75(76)	78(79)
	A'	CCI bend	135(134)	127	130	114(113)	114(113)	117(115)	115(114)	122(121)
	A"	CF_2 twist	227(225)	212	229	211(208)	210(192)	209(211)	211(209)	216(214)
	A'	C-I stretch	285(286)	290	259	234(231)	243(241)	254(252)	237(235)	272(272)
	A"	CF_2 twist	292(292)	274	279	259(259)	262(259)	266(266)	260(260)	275(275)
	A'	CF_2 scissor	396(374)	368	397	366(364)	368(366)	370(369)	367(365)	374(372)
	A"	CF_2 rock	558(558)	515	556	510(510)	513(511)	517(517)	512(511)	526(525)
	A'	CF_2 wag	618(610)	568	608	538(530)	544(536)	555(547)	542(533)	566(559)
	A'	CF_2 scissor	638(627)	602	628	569(565)	575(570)	580(576)	571(567)	590(583)
	A'	CF_2 scissor	730(725)	679	726	645(631)	653(639)	664(653)	649(636)	677(668)
	A'	symm C-F stretch + C-C twist	980(964)	954	1003	792(765)	809(782)	833(806)	800(773)	868(842)
	A'	symm C-F stretch	1262(1232)	1149	1265	1126(1097)	1144(1117)	1162(1135)	1132(1103)	1178(1150)
	A"	asymm C-F stretch	1338(1300)	1184	1348	1163(1125)	1189(1154)	1211(1177)	1170(1132)	1231(1195)
	A"	asymm C-F stretch	1433(1395)	1302	1429	1289(1126)	1316(1283)	1336(1302)	1296(1261)	1340(1304)
	A'	symm C-F stretch + C-C stretch	1496(1485)	1387	1496	1372(1365)	1392(1385)	1409(1401)	1377(1370)	1435(1428)
***Gauche* (C_1)**	A	torsion	67(68)	64	69	56(58)	57(58)	57(61)	56(58)	61(62)
	A	CCI bend	147(147)	138	142	131(131)	131(130)	133(133)	131(131)	140(140)
	A	CF_2 twist	246(242)	224	246	215(212)	214(211)	215(212)	216(213)	219(215)
	A	C-I stretch	291(290)	272	262	257(257)	261(260)	265(264)	258(258)	273(272)
	A	FCI bend	298(298)	285	283	266(267)	272(273)	277(278)	268(268)	288(288)
	A	CF_2 wag	323(321)	301	319	294(293)	295(294)	297(295)	295(293)	303(301)
	A	CF_2 scissor	478(477)	441	477	434(432)	437(437)	442(440)	436(434)	449(447)
	A	CF_2 scissor	625(619)	571	623	566(560)	571(565)	576(571)	568(562)	581(575)
	A	CF_2 scissor	680(675)	626	675	605(602)	611(606)	619(616)	608(605)	628(625)
	A	C-C twist	867(859)	794	870	751(745)	757(751)	769(764)	755(749)	786(780)
	A	C-F stretch + C-C twist	1030(1014)	957	1010	900(885)	913(895)	931(915)	906(891)	967(951)

	A	C-F stretch + C-C twist	1228(1195)	1092	1239	1037(991)	1062(1020)	1086(1046)	1045(999)	1114(1073)
	A	asymm C-F stretch	1305(1263)	1161	1322	1129(1089)	1153(1116)	1175(1137)	1136(1096)	1196(1158)
	A	asymm C-F stretch	1409(1369)	1280	1406	1249(1214)	1277(1243)	1299(1264)	1257(1221)	1313(1277)
	A	symm C-F stretch + C-C stretch	1477(1464)	1364	1481	1320(1312)	1343(1335)	1364(1355)	1327(1318)	1399(1391)
Bridge (C_{2v})	B_2	shuttle along CC	-	824*i*	1582*i*	413*i*(431*i*)	408*i*(427*i*)	432*i*(452*i*)	424*i*(444*i*)	560*i*(586*i*)
	A_2	CF_2 twist		67	16	21*i*(28)	14*i*(33)	5(35)	21*i*(30)	33*i*(19*i*)
	B_1	shuttle perp. to CC		194	151	163(165)	167(169)	169(171)	163(166)	164(163)
	A_1	I-(C_2F_4) stretch		226	127	169(172)	178(179)	181(182)	170(172)	178(178)
	B_1	CF_2 rock		220	242	215(214)	213(212)	213(212)	215(215)	219(218)
	A_1	CF_2 wag		331	332	308(307)	312(311)	315(314)	310(308)	321(318)
	A_2	C-C twist + CF_2 rock		441	504	441(440)	443(443)	449(448)	443(443)	459(459)
	B_2	CF_2 scissor		472	497	499(496)	505(502)	507(504)	499(496)	493(489)
	A_1	CF_2 scissor		601	611	570(559)	578(567)	583(571)	571(560)	582(571)
	B_2	C-C twist		668	802	643(638)	654(648)	661(654)	646(640)	657(649)
	A_1	symm C-F stretch		855	957	851(828)	861(839)	873(851)	855(833)	896(876)
	B_2	symm C-F stretch		1009	1155	1049(1015)	1068(1036)	1085(1054)	1055(1021)	1092(1064)
	A_2	asymm C-F stretch		1197	1390	1189(1155)	1215(1183)	1239(1209)	1197(1163)	1259(1230)
	B_1	asymm C-F stretch		1212	1391	1197(1142)	1224(1172)	1250(1199)	1205(1150)	1272(1222)
	A_1	symm C-F stretch + C-C stretch		1392	1517	1326(1304)	1352(1330)	1378(1356)	1335(1312)	1423(1401)

Table S8. The performance of methods for various molecular properties.[a]

	HF	MP2	CAS(12,12)	CASPT2	B3LYP	B3PW91	PBE0	X3LYP	M05-2X
r(C-I)	△	◎	X	◎	X	X	△	X	O
r(C-F)	X	O	X	O	O	O	◎	O	O
r(C-C)	O	O	◎	◎	△	△	O	△	◎
∠CCF	O	O	O	O	O	O	O	O	O
∠FCF	O	O	O	O	O	O	O	O	O
∠CCI	O	O	O	O	O	O	O	O	O
∠CCI	△	O	△	O	O	O	O	O	O
[b]∠ICCI	O	△	O	O	O	O	O	O	O
[c]Avg.	2.5	3.0	2.5	3.3	2.6	2.6	3.0	2.6	3.1
[d]$\Delta E_{gauche\text{-anti}}$	△	△	O	O	O	◎	◎	O	◎
Vib. Freq.	X	△	X	-	◎	◎	O	◎	△
T_v	-	-	-	◎	X	△	△	X	◎

a: (Best) ◎(4) → O(3) → △(2) → X(1) (Worst)

b: the bond angle in the gauche structure of CF_2ICF_2I

c: the average score of the performance for the prediction of molecular structure

d: the energy difference between the anti and the gauche structure in CF_2ICF_2I

Table S9. Optimized geometries (bond lengths in Å and bond angles in degrees) of CF_2ICF_2I and relative energies between anti and gauche structures in the gas phase.

CF_2ICF_2I /Gas	Geom.	PBE
Anti (C_{2h}, ^1A_g)	C-C	1.557
	C-F	1.349
	C-I	2.196
	∠CCF	110.66
	∠FCF	108.78
	∠CCI	110.66
Gauche **(C_2, ^1A)**	C-C	1.568
	C-F	1.356
	C-F′	1.349
	C-I	2.182
	∠CCF	107.62
	∠CCF′	109.42
	∠FCF	107.90
	∠CCI	112.81
	∠ICCI	66.47
$\Delta E_{gauche\text{-}anti}$ (kcal/mol)		1.86

Table S10. Vibrational frequencies (cm^{-1}) of CF_2ICF_2I in the gas phase

CF_2ICF_2I	mode	PBE
Anti (C_{2h})	A_u	45
	B_u	97
	A_g	125
	A_u	207
	B_g	246
	A_g	254
	B_u	271
	A_u	272
	A_g	348
	B_g	495
	B_u	555
	A_g	652
	B_u	666
	A_g	911
	B_u	1076
	B_g	1105
	A_u	1117
	A_g	1171
***Gauche* (C_2)**	A	49
	A	87
	B	150
	B	228
	A	238
	B	267
	A	271
	A	289
	B	318
	A	430
	B	564
	A	617

B	799
A	924
B	1030
A	1085
B	1102
A	1149

Table S11. The vertical excitation energies (T_v in eV) and oscillator strengths (in parenthesis, × 10^{-3}) of CF_2ICF_2I in the gas phase.

CF_2ICF_2I	State	PBE
Anti (C_{2h})	^3B_u	3.16
	^3A_u	3.19
	^3B_g	3.30
	^3A_g	3.43
	^1B_u	3.58(10.6)
	^1A_u	3.59
	^1B_g	3.71
	^1A_g	3.83
***Gauche* (C_2)**	$^3B(1)$	3.44
	$^3A(1)$	3.55
	$^3A(2)$	3.64
	$^3B(2)$	3.70
	$^1B(1)$	3.80(2.6)
	$^1A(2)$	3.91(0.4)
	$^1A(3)$	3.80
	$^1B(2)$	4.07

Table S12. Optimized geometries (bond lengths in Å and bond angles in degrees) of •CF_2CF_2I radical and relative energies in the gas phase.

•CF_2CF_2I /Gas	Geom.	PBE
Anti (C_s, $^2A'$)	C-C	1.490
	C-F	1.349
	C-F′	1.324
	C-I	2.260
	∠CCF	110.62
	∠CCF′	116.92
	∠FCF	109.57
	∠F′CF′	112.57
	∠CCI	110.84
Gauche **(C_1, ^2A)**	C-C	1.512
	C-F_1	1.368
	C-F_2	1.352
	C-F_3	1.336
	C-F_4	1.331
	C-I	2.185
	∠CCF_1	112.03
	∠CCF_2	108.95
	∠CCF_3	114.63
	∠CCF_4	115.75
	∠F_1CF_2	107.47
	∠F_3CF_4	111.43
	∠CCI	109.50
$\Delta E_{gauche\text{-anti}}$ (kcal/mol)		4.19
Bridge (C_{2v}, $^2B_2$)	C-C	1.552
	C-F	1.341
	C-I	2.418
	∠CCF	115.25

∠ FCF	109.98
∠ CCI	71.28
$\Delta E_{bridge\text{-}anti}$ (kcal/mol)	25.47

Table S13. Vibrational frequencies (cm^{-1}) of $•CF_2CF_2I$ in the gas phase.

$•CF_2CF_2I$	mode	PBE
Anti (C_s)	A"	74
	A'	107
	A"	203
	A'	217
	A"	248
	A'	356
	A"	494
	A'	511
	A'	548
	A'	608
	A'	752
	A'	1090
	A"	1122
	A"	1255
	A'	1345
***Gauche* (C_1)**	A	54
	A	126
	A	202
	A	247
	A	257
	A	285
	A	420
	A	546
	A	581
	A	715
	A	861
	A	979
	A	1085
	A	1205
	A	1277

Bridge (C_{2v})	B_2	287*i*
	A_2	33*i*
	B_1	159
	A_1	173
	B_1	206
	A_1	300
	A_2	418
	B_2	492
	A_1	557
	B_2	631
	A_1	824
	B_2	1009
	A_2	1132
	B_1	1143
	A_1	1270

Table S14. The vertical excitation energies (T_v in eV) and oscillator strengths (in parenthesis, × 10^{-3}) of •CF_2CF_2I in the gas phase.

•CF_2CF_2I	State	Characteristics	PBE
Anti (C_s)	**^{2}A″(1)**	n → SOMO	2.23
	^{2}A′(2)	n → SOMO	2.32(2.0)
	^{2}A′(3)	SOMO → σ*	3.45(36.3)
	^{2}A″(2)	n → σ*	3.96
	^{2}A′(4)	n → σ*	4.03(0.6)
***Gauche* (C_1)**	**^{2}A(2)**	SOMO → σ*	3.02(0.4)
	^{2}A(3)	n → SOMO	3.08(0.3)
	^{2}A(4)	n → SOMO	3.15(12.0)
	^{2}A(5)	n → σ*	3.70
	^{2}A(6)	n → σ*	3.76(0.1)
	^{2}A(7)	n → σ*	4.38(0.1)

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