Supplementary Information.

Table S1. NPA Charges on Atoms in Substituted Staggered 1,1,1-Trifluoroethanes

X	F_{ap}	F_g	C of CF_3	H of CH_2	C of CH_2	X
F	-0.414	-0.407	1.199	0.212	0.026	-0.420
SO_2F	-0.405	-0.398	1.243	0.295	-0.775	0.142
OH	-0.419	-0.409	1.223	0.209	-0.110	-0.291
CF_3	-0.412	-0.406	1.246	0.274	-0.594	0.022
H	-0.419	-0.419	1.233	0.247	-0.715	0.247
NH_2	-0.416	-0.422	1.220	0.238	-0.302	-0.135
NF_2	-0.414	-0.402	1.232	0.267	-0.344	-0.206
SiH_3	-0.417	-0.419	1.241	0.268	-0.988	0.468
SiF_3	-0.412	-0.412	1.246	0.283	-1.097	0.521
CH_3	-0.418	-0.421	1.240	0.246	-0.518	0.044
CH_2Li	-0.433	-0.427	1.232	0.223	-0.517	0.125
CH_2F[a]	-0.416	-0.408[b]	1.242	0.260[b]	-0.558	0.048
		-0.421		0.253		
CH_2F[c]	-0.411	-0.418	1.240	0.257	-0.555	0.050
CH_2^-	-0.459	-0.441	1.218	0.208	-0.530	-0.764
CF_2^-	-0.456	-0.425	1.236	0.228	-0.612	-0.744
BH_3^-	-0.460	-0.436	1.237	0.212	-0.756	-0.573
BF_3^-	-0.455	-0.430	1.241	0.224	-0.870	-0.508
$B(OH)_3^-$	-0.456	-0.440[d]	1.243	0.217[d]	-0.896	-0.513
		-0.434[d]		0.229[d]		
NH_3^+	-0.371	-0.401	1.233	0.287	-0.301	0.668
NF_3^+	-0.367	-0.380	1.241	0.313	-0.288	0.550
OH_2^+	-0.367	-0.397	1.214	0.286	-0.106	0.482

[a]The fluorine atom is gauche to the C-C bond of the trifluoroethane group. [b]Same side of the plane defined by the three carbons of the molecule as is the fluorine atom of the CH_2F group. [c]The fluorine atom is antiperiplanar to the C-C bond of the trifluoroethane group. [d]The orientation of the hydrogens on the oxygens remove the plane of symmetry from this species.

Table S2. NPA Charges on Atoms in Substituted Eclipsed 1,1,1-Trifluoroethanes

X	F_{syn}	F_g	C of CF_3	H of CH_2	C of CH_2	X
F	-0.398	-0.415	1.194	0.212	0.027	-0.418
SO_2F	-0.400	-0.404	1.244	0.299	-0.775	0.083
OH	-0.398	-0.420	1.218	0.209	-0.111	-0.289
CF_3	-0.403	-0.411	1.246	0.276	-0.596	0.023
H	-0.419	-0.419	1.230	0.251	-0.724	0.251
NH_2	-0.420	-0.420	1.214	0.242	-0.306	-0.132
NF_2	-0.395	-0.412	1.230	0.269	-0.342	-0.206
SiH_3	-0.421	-0.417	1.241	0.273	-1.001	0.468
SiF_3	-0.417	-0.411	1.246	0.288	-1.107	0.522
CH_3	-0.419	-0.420	1.238	0.249	-0.524	0.046
CH_2Li	-0.421	-0.433	1.227	0.227	-0.523	0.128
CH_2^-	-0.432	-0.455	1.210	0.213	-0.539	-0.757
CF_2^-	-0.411	-0.448	1.234	0.232	-0.616	-0.774
BH_3^-	-0.427	-0.453	1.235	0.218	-0.770	-0.569
BF_3^-	-0.421	-0.446	1.241	0.230	-0.882	-0.506
$B(OH)_3^-$	-0.434	-0.450[a]	1.242	0.224[a]	-0.850	-0.517
		-0.446[a]		0.231[a]		
NH_3^+	-0.412	-0.382	1.234	0.288	-0.305	0.670
NF_3^+	-0.388	-0.373	1.243	0.313	-0.285	0.551
OH_2^+	-0.405	-0.378	1.214	0.287	-0.111	0.486

[a]The orientation of the hydrogens on the oxygens remove the plane of symmetry from this species.

Table S3. NPA Charges on Atoms in Eclipsed CH_3CH_2X

X	H_{syn}	H_g	C of CH_3	H of CH_2	C of CH_2	X
F	0.246	0.225	-0.697	0.186	0.083	-0.452
SO_2F	0.241	0.244	-0.655	0.276	-0.697	0.071
OH	0.243	0.220	-0.671	0.180	-0.048	-0.325
CF_3	0.238	0.232	-0.657	0.248	-0.523	-0.018
H	0.219	0.219	-0.658	0.219	-0.658	0.219
NH_2	0.216	0.220	-0.648	0.213	-0.241	-0.171
NF_2	0.250	0.231	-0.679	0.241	-0.268	-0.246
SiH_3	0.212	0.226	-0.641	0.245	-0.948	0.428
SiF_3	0.224	0.232	-0.647	0.263	-1.059	0.490
CH_3	0.215	0.220	-0.648	0.217	-0.454	0.011
CH_2Li	0.214	0.205	-0.648	0.194	-0.455	0.091
CH_2^-	0.207	0.177	-0.658	0.181	-0.471	-0.793
CF_2^-	0.233	0.187	-0.654	0.198	-0.540	-0.807
BH_3^-	0.206	0.181	-0.628	0.180	-0.702	-0.597
BF_3^-	0.217	0.187	-0.632	0.194	-0.809	-0.538
$B(OH)_3^-$	0.213	0.181[a]	-.626	0.184[a]	-0.774	-0.555
		0.183[a]		0.194[a]		
NH_3^+	0.235	0.268	-0.690	0.261	-0.233	0.629
NF_3^+	0.266	0.280	-0.705	0.288	-0.199	0.502
OH_2^+	0.251	0.274	-0.718	0.262	-0.028	0.424

[a]The orientation of the hydrogens on the oxygens remove the plane of symmetry from this species.

Table S4. Numerical Values of the Potential Gradient for CH_3CH_2X[a]

X	Position	γ (AIM)	γ (NPA)	X	Position	γ (AIM)	γ (NPA)
F	ap	0.0045	-0.0531	e-CF_3	syn	0.1108	0.0208
	g	0.0742	-0.0109		g	0.0617	-0.0141
OH	ap	-0.0140	-0.0519	H	ap	0.0052	
	g	0.0649	0.0096		g	0.0052	
CH_3	ap	0.0123	-0.0573	e-CH_2Li	syn	0.0155	-0.0363
	g	0.0116	-0.0447		g	-0.0275	-0.0870
CF_3	ap	0.0479	-0.0233	NF_2	ap	0.0005	-0.0424
	g	0.0965	0.0106		g	0.0971	0.0236
e-F	syn	0.1109	0.0614	CH_2Fin	ap	0.014	-0.0523
	g	0.0224	-0.0087		gs	0.0859	0.0134
e-OH	syn	0.1121	0.0454		go	0.007	-0.0518
	g	0.0062	-0.0363	CH_2Fout	ap	0.0456	-0.0260
NH_2	ap	0.0234	-0.0367		g	0.0222	-0.0375
	g	0.0408	-0.0260	CF_2H	ap	0.0073	-0.0505
CH_2Li	ap	-0.0345	-0.0964		g	0.0785	0.0050
	g	-0.0048	-0.0584	e-CF_2H[b]	ap	0.0637	
SiH_3	ap	0.0195	-0.0549		g	0.0466	
	g	-0.0444	-0.0725	e-CH_3	syn	-0.0011	-0.0567
SiF_3	ap	0.0272	-0.0224		g	0.0012	-0.0453
	g	-0.0288	-0.0310	NH_3^+	ap	0.0812	0.0708
e-SiF_3	syn	-0.0659	-0.0567		g	0.0534	0.0220
	g	0.0136	-0.0268	BH_3^-	ap	-0.0755	-0.1774
SO_2F	ap	0.0638	-0.0021		g	-0.052	-0.0993
	g	0.1143	0.0221	NF_3^+	ap	0.1064	0.0962
e-SO_2F	syn	0.061			g	0.1129	0.0812
	g	0.0992		CH_2^-	ap	-0.0930	-0.1709
e-SiH_3	syn	-0.0822	-0.0856		g	-0.0329	-0.0923
	g	0.0042	-0.0601	CF_2^-	ap	-0.1134	-0.1786
Cl	ap	-0.0110	-0.0492		g	0.0266	-0.0424
	g	0.0256	-0.0196	e-NH_3^+	syn	0.0421	-0.0030
e-NF_3^+	syn	0.111	0.0654		g	0.0842	0.0575
	g	0.1114	0.0931	BF_3^-	ap	-0.0672	-0.1427
e-CH_2^-	syn	-0.0062	-0.0567		g	-0.034	-0.0613
	g	-0.0775	-0.1487	OH_2^+	ap	0.0927	0.0928
e-CF_2^-	syn	0.0597	0.0222		g	0.0522	0.0480
	g	-0.0784	-0.1435	e-BF_3^-	syn	-0.0308	-0.0333
O^-	ap	-0.0677	-0.1451		g	-0.057	-0.1206
	g	0.0435	-0.0432	e-BH_3^-	syn	-0.0493	-0.0665
PH_3^+	ap	0.0694	0.0551		g	-0.0683	-0.1566
	g	-0.0082	-0.0221				

[a]An "e" in front of the X group designation indicates the eclipsed conformer. [b]The hydrogen atom in X is eclipsed with the C-C bond of the ethyl moeity.

Table S5. The Potential Gradient Values for CF_3CH_2X[a]

X	Position	γ (AIM)	γ (NPA)	X	Position	γ (AIM)	γ (NPA)
F	ap	0.0159	-0.0391	e-CF_3	syn	0.1132	0.0581
	g	0.1143	0.0355		g	0.0794	0.0157
OH	ap	-0.0045	-0.0692	H	ap	0.0374	-0.0487
	g	0.1080	0.0152		g	0.0374	-0.0487
CH_3	ap	0.0432	-0.0680	e-CH_2Li	syn	0.0441	-0.0283
	g	0.0357	-0.0443		g	0.0025	-0.0931
CF_3	ap	0.0760	-0.0305	NF_2	ap	0.0158	-0.0563
	g	0.1077	-0.0007		g	0.1283	0.0191
e-F	syn	0.1535	0.0665	CH_2Fin	ap	0.0420	-0.0597
	g	0.0447	-0.0170		gs	0.1027	0.0080
e-OH	syn	0.1562	0.0530		go	0.0192	-0.0571
	g	0.0273	-0.0446	CH_2Fout	ap	0.0803	-0.0282
NH_2	ap	0.0449	-0.0478		g	0.0380	-0.0392
	g	0.0722	-0.0257	e-NH_3^+	syn	0.0631	-0.0160
CH_2Li	ap	-0.0050	-0.1106		g	0.1019	0.0468
	g	0.0281	-0.0543	e-CH_3	syn	0.0309	-0.0331
SiH_3	ap	0.0711	-0.0570		g	0.0379	-0.0605
	g	-0.0260	-0.0805	NH_3^+	ap	0.1148	0.0653
SiF_3	ap	0.0746	-0.0164		g	0.0760	0.0042
	g	-0.0158	-0.0559	BH_3^-	ap	-0.0240	-0.1870
e-SiF_3	syn	0.0243	-0.0586		g	-0.0177	-0.1026
	g	0.0530	-0.0486	e-SiH_3	syn	-0.0738	-0.0942
SO_2F	ap	0.0939	-0.0040		g	0.0439	-0.0637
	g	0.1092	-0.0015				

[a]See note *a* of Table S4.

Table S6. The Potential Gradient (AIM Method) for Fluorine Atoms in Compounds of the Type $CF_3(CH_2)_nNH_3^{+a}$

Compound	Position	γ (AIM)
$CF_3CH_2NH_3^+$	ap	0.0978
	g	0.0454
e-$CF_3CH_2NH_3^+$	syn	0.0261
	g	0.0808
$CF_3(CH_2)_2NH_3^+$	ap	0.0382
	g	0.0094
$CF_3(CH_2)_4NH_3^+$	ap	0.0520
	g	0.0041
$CF_3(CH_2)_4NH_3^{+b}$	a	-0.0248
	b	0.0829
	c	0.0195

[a]An e before the compound indicates an eclipsed conformer. [b]Twisted conformer as illustrated in Figure 2.