Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Axial-Equatorial Isomerism and Semiexperimental Equilibrium Structures of Fluorocyclohexane

ELECTRONIC SUPPORTING INFORMATION

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Table S1. Experimental rotational transitions (obs) for the equatorial parent species of fluorocyclohexane, along with observed minus calculated values (o-c) and transition uncertainties (unc, all values in MHz).

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	obs	o-c	unc
2	1	2	1	1	1	6963.61910	0.0000	0.005
2	0	2	1	0	1	7451.64790	0.0016	0.005
2	1	1	1	1	0	8157.97270	0.0044	0.005
2	2	1	2	0	2	9801.80210	0.0003	0.005
3	1	3	2	1	2	10382.4615	0.0005	0.005
3	0	3	2	0	2	10926.7235	-0.0090	0.005
3	1	2	2	1	1	12161.2644	0.0020	0.005
3	2	2	2	2	1	11341.1840	0.0036	0.005
3	2	1	2	2	0	11755.6368	0.0016	0.005
4	0	4	3	0	3	14196.6962	-0.0007	0.005
4	1	4	3	1	3	13741.8724	0.0008	0.005
4	1	3	3	1	2	16055.9745	-0.0047	0.005
4	2	3	3	2	2	15035.9686	0.0012	0.005
4	2	2	3	2	1	15959.4600	-0.1587	0.250
4	3	2	3	3	1	15306.9033	-0.0010	0.005
4	3	1	3	3	0	15381.4936	-0.0014	0.005
5	0	5	4	0	4	17346.6561	0.0009	0.005
5	1	5	4	1	4	17043.8351	0.0021	0.005
5	1	4	4	1	3	19781.4400	-0.0247	0.250
5	2	4	4	2	3	18660.0300	-0.0625	0.250
5	2	3	4	2	2	20205.7000	-0.0253	0.250
5	3	3	4	3	2	19163.2800	0.0126	0.250
5	3	2	4	3	1	19411.2400	-0.1618	0.250
6	0	6	5	0	5	20470.8300	-0.0369	0.250
6	1	6	5	1	5	20299.3900	0.0529	0.250
6	1	5	5	1	4	23280.9200	-0.0573	0.250
6	2	5	5	2	4	22202.1600	-0.0979	0.250
6	2	4	5	2	3	24371.3900	0.0198	0.250
6	3	4	5	3	3	22997.1000	0.0603	0.250
6	3	3	5	3	2	23597.2800	-0.1118	0.250

Table S2. Experimental rotational transitions (obs) for the equatorial $^{13}C(1)$ species of fluorocyclohexane, along with observed minus calculated values (o-c) and transition uncertainties (unc, all values in MHz).

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	obs	o-c	unc
3	1	3	2	1	2	10350.7784	-0.0005	0.005
3	0	3	2	0	2	10893.4825	0.0000	0.005
4	1	4	3	1	3	13701.1600	-0.0012	0.005
3	1	2	2	1	1	12115.3837	0.0028	0.005
4	0	4	3	0	3	14156.9407	0.0000	0.005
4	2	3	3	2	2	14984.1287	0.0013	0.005
4	1	3	3	1	2	15997.8232	-0.0031	0.005
5	0	5	4	0	4	17299.9917	0.0009	0.005

Table S3. Experimental rotational transitions (obs) for the equatorial $^{13}C(2)$ species of fluorocyclohexane, along with observed minus calculated values (o-c) and transition uncertainties (unc, all values in MHz).

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	obs	o-c	unc
2	1	2	1	1	1	6938.4006	-0.0012	0.005
2	0	2	1	0	1	7428.5891	0.0003	0.005
2	1	1	1	1	0	8147.3254	0.0022	0.005
3	1	3	2	1	2	10341.8332	-0.0012	0.005
4	1	4	3	1	3	13683.7583	-0.0006	0.005
4	0	4	3	0	3	14126.5887	-0.0007	0.005
4	2	3	3	2	2	14996.0330	-0.0001	0.005
4	1	3	3	1	2	16020.8474	-0.0034	0.005
3	0	3	2	0	2	10881.8398	0.0001	0.005
3	1	2	2	1	1	12141.4226	0.0029	0.005
5	1	5	4	1	4	16966.9643	0.0009	0.005
5	0	5	4	0	4	17255.2691	0.0014	0.005

Table S4. Experimental rotational transitions (obs) for the equatorial $^{13}C(3)$ species of fluorocyclohexane, along with observed minus calculated values (o-c) and transition uncertainties (unc, all values in MHz).

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	obs	o-c	unc
2	0	2	1	0	1	7389.7362	0.0014	0.005
3	1	3	2	1	2	10290.7526	-0.0012	0.005
4	1	4	3	1	3	13618.0148	-0.0012	0.005
4	0	4	3	0	3	14063.7235	-0.0006	0.005
4	2	3	3	2	2	14914.7585	0.0009	0.005
4	1	3	3	1	2	15931.6926	-0.0032	0.005
3	0	3	2	0	2	10829.6576	0.0000	0.005
3	1	2	2	1	1	12070.9080	0.0030	0.005
5	1	5	4	1	4	16887.4521	0.0002	0.005
5	0	5	4	0	4	17180.5736	0.0014	0.005

Table S5. Experimental rotational transitions (obs) for the equatorial $^{13}C(4)$ species of fluorocyclohexane, along with observed minus calculated values (o-c) and transition uncertainties (unc, all values in MHz).

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	obs	o-c	unc
3	1	3	2	1	2	10250.5207	-0.0016	0.005
4	1	4	3	1	3	13571.7168	-0.0009	0.005
4	0	4	3	0	3	14032.4870	-0.0004	0.005
4	2	3	3	2	2	14826.3496	0.0016	0.005
4	1	3	3	1	2	15825.1094	-0.0032	0.005
3	0	3	2	0	2	10790.7679	0.0000	0.005
3	1	2	2	1	1	11979.5191	0.0030	0.005
5	1	5	4	1	4	16837.7714	0.0003	0.005
5	0	5	4	0	4	17152.1730	0.0012	0.005

Table S6. Experimental rotational transitions (obs) for the axial parent species of fluorocyclohexane, along with observed minus calculated values (o-c) and transition uncertainties (unc, all values in MHz).

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	obs	o-c	unc
1	1	0	0	0	0	6191.5922	0.0046	0.005
2	0	2	1	1	0	7398.1392	-0.0027	0.005
2	1	2	1	1	1	8571.2592	0.0016	0.005
2	0	2	1	0	1	8980.2265	-0.0003	0.005
2	1	1	1	1	0	9866.7399	0.0027	0.005
2	1	1	1	0	1	11448.8280	0.0059	0.005
3	1	3	2	1	2	12727.2443	0.0007	0.005
2	2	0	1	1	0	12908.5440	-0.0032	0.005
3	0	3	2	0	2	13030.3699	-0.0018	0.005
2	2	1	1	1	1	13317.5180	-0.0006	0.005
3	2	2	2	2	1	13828.4839	0.0035	0.005
3	1	2	2	1	1	14610.7782	-0.0089	0.005
3	2	1	2	2	0	14626.5756	-0.0006	0.005
4	0	4	3	0	3	16937.3377	0.0013	0.005
4	1	4	3	1	3	16792.6407	0.0013	0.005
3	1	2	2	0	2	17079.36	-0.0223	0.250
3	2	1	2	1	1	17668.32	-0.0663	0.250
4	2	3	3	2	2	18245.85	-0.0020	0.250
3	2	2	2	1	2	18574.71	-0.0313	0.250
4	3	2	3	3	1	18787.74	-0.0027	0.250
4	1	3	3	1	2	19062.96	-0.0458	0.250
4	3	1	3	3	0	19108.31	-0.0254	0.250
4	2	2	3	2	1	19734.16	-0.0231	0.250
3	3	1	2	2	1	20249.13	-0.0693	0.250
3	3	0	2	2	0	20070.09	-0.0167	0.250
4	2	2	3	1	2	22791.77	-0.0123	0.250
4	1	3	3	0	3	23111.99	-0.0264	0.250
4	2	3	3	1	3	24093.32	-0.0298	0.250
4	3	1	3	2	1	24551.86	-0.0059	0.250
4	3	2	3	2	2	25208.39	-0.0717	0.250
4	4	1	3	3	1	27307.97	-0.0064	0.250
4	4	0	3	3	0	27260.52	-0.0228	0.250

Table S7. Experimental rotational transitions (obs) for the axial $^{13}C(1)$ species of fluorocyclohexane, along with observed minus calculated values (o-c) and transition uncertainties (unc, all values in MHz).

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	obs	o-c	unc
2	0	2	1	0	1	8933.1159	-0.0011	0.005
3	1	3	2	1	2	12663.3422	-0.0008	0.005
3	0	3	2	0	2	12970.6585	-0.0011	0.005
3	1	2	2	1	1	14520.2438	0.0005	0.005
4	1	4	3	1	3	16712.1335	0.0004	0.005
4	0	4	3	0	3	16862.0742	0.0011	0.005

Table S8. Experimental rotational transitions (obs) for the axial $^{13}C(2)$ species of fluorocyclohexane, along with observed minus calculated values (o-c) and transition uncertainties (unc, all values in MHz).

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	obs	o-c	unc
2	0	2	1	0	1	8930.6015	0.0020	0.005
3	1	3	2	1	2	12654.7293	0.0000	0.005
2	2	0	1	1	0	12760.1239	0.0000	0.005
3	0	3	2	0	2	12943.4929	-0.0007	0.005
3	1	2	2	1	1	14552.5420	-0.0005	0.005
4	1	4	3	1	3	16690.2803	0.0004	0.005
4	0	4	3	0	3	16822.2801	-0.0005	0.005

Table S9. Experimental rotational transitions (obs) for the axial $^{13}C(3)$ species of fluorocyclohexane, along with observed minus calculated values (o-c) and transition uncertainties (unc, all values in MHz).

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	obs	o-c	unc
2	0	2	1	0	1	8905.9118	0.0026	0.005
3	1	3	2	1	2	12616.0384	0.0003	0.005
2	2	0	1	1	0	12775.0309	0.0001	0.005
3	0	3	2	0	2	12910.3267	-0.0020	0.005
3	1	2	2	1	1	14511.1120	-0.0006	0.005
4	1	4	3	1	3	16640.5055	0.0004	0.005
4	0	4	3	0	3	16777.1551	0.0000	0.005

Table S10. Experimental rotational transitions (obs) for the axial $^{13}C(4)$ species of fluorocyclohexane, along with observed minus calculated values (o-c) and transition uncertainties (unc, all values in MHz).

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	obs	o-c	unc
2	0	2	1	0	1	8861.5551	0.0008	0.005
3	1	3	2	1	2	12559.1457	-0.0010	0.005
3	0	3	2	0	2	12875.9875	-0.0018	0.005
3	1	2	2	1	1	14393.6799	0.0001	0.005
4	1	4	3	1	3	16578.6833	0.0003	0.005
4	0	4	3	0	3	16738.5748	0.0013	0.005

Table S11. Born-Oppenheimer equilibrium structure, r_e^{BO}, of cyclohexanone (distances in Å and angles in degree).

Parameter	Value[a]	Parameter	Value[a]
C1C2	1.5124	C2C3Hq	109.66
C2C3	1.5332	C2C3Ha	109.04
C3C4	1.5256	C3C4Hq	110.11
C1O	1.2126	C3C4Ha	109.35
C2Hq	1.0877	HqC2Ha	108.38
C2Ha	1.0944	HqC3Ha	106.92
C3Hq	1.0900	HaC4Hq	106.95
C3Ha	1.0931		
C4Hq	1.0905	C1C2C3C4	53.46
C4Ha	1.0942	C2C3C4C5	-57.37
		C6C1C2C3	-51.63
C1C2C3	110.80	OC1C2C3	127.19
C2C3C4	111.18	OC1C2Hq	3.43
C3C4C5	110.89	OC1C2Ha	-113.79
C2C1C6	114.98	C1C2C3Hq	176.24
C2C1O	122.50	C1C2C3Ha	-67.00
C1C2Hq	108.69	C2C3C4Hq	-179.48
C1C2Ha	107.69	C2C3C4Ha	63.28

[a]Estimated according to the equation: $r_e^{BO} = r_e$[CCSD(T)/cc-pVTZ] + r_e[MP2/cc-pVQZ] – r_e[MP2/cc-pVTZ] + r_e[MP2_AE/cc-pwCVQZ] – r_e[MP2/cc-pwCVQZ]

Table S12. Ab initio structures of cyclohexanone (distances in Å and angles in degree).

Method Basis set	CCSD(T)_FC cc-pVTZ	MP2_FC cc-pVQZ	MP2_FC cc-pVTZ	MP2_AE cc-pwCVQZ	MP2_FC cc-pwCVQZ	r_e^{BO}
C4Ha	1.0968	1.0928	1.0938	1.0911	1.0928	1.0942
C1C4	2.9257	2.9043	2.9083	2.8973	2.9036	2.9155
C1C2	1.5186	1.5087	1.5113	1.5046	1.5083	1.5124
C2C3	1.5390	1.5316	1.5337	1.5275	1.5312	1.5332
C1O	1.2169	1.2167	1.2188	1.2141	1.2163	1.2126
C4Hq	1.0931	1.0895	1.0905	1.0878	1.0895	1.0905
C2Hq	1.0901	1.0869	1.0878	1.0852	1.0868	1.0877
C2Ha	1.0970	1.0929	1.0938	1.0912	1.0929	1.0944
C3Hq	1.0926	1.0891	1.0901	1.0874	1.0890	1.0900
C3Ha	1.0958	1.0918	1.0929	1.0901	1.0918	1.0931
C1C4Ha	99.945	100.166	100.203	100.185	100.165	99.927
C4C1C2	59.924	60.069	60.058	60.059	60.066	59.929
C1C2C3	110.722	110.243	110.203	110.291	110.251	110.802
C4C1O	157.504	155.937	155.727	156.064	155.970	157.808
HqC4Ha	106.991	106.952	106.955	106.910	106.948	106.950
C1C2Hq	108.642	108.800	108.742	108.791	108.801	108.691
C1C2Ha	107.810	108.038	108.149	108.017	108.028	107.688
C2C3Hq	109.700	109.685	109.740	109.696	109.684	109.657
C2C3Ha	109.027	109.021	109.010	109.031	109.025	109.044
HaC4C1C2	-76.868	-76.330	-76.208	-76.373	-76.338	-77.024
C4C1C2C3	-27.023	-27.273	-27.335	-27.245	-27.271	-26.936
C4C1C2Hq	-150.661	-150.761	-150.730	-150.775	-150.770	-150.698
C4C1C2Ha	92.024	91.556	91.549	91.619	91.560	92.090
C1C2C3Hq	176.374	177.071	177.175	177.036	177.063	176.243
C1C2C3Ha	-66.778	-66.155	-66.000	-66.238	-66.170	-67.001

Table S13. Ab initio structures of equatorial fluorocyclohexane (distances in Å and angles in degree).

Method Basis set	CCSD(T)_AE cc-pwCVTZ	MP2_AE cc-pwCVQZ	MP2_AE cc-pwCVTZ	r_e^{BO}[a]
C1Fq	1.3926	1.3943	1.3924	1.3945
C2Ha	1.0938	1.0899	1.0907	1.0930
C1Ha	1.0948	1.0913	1.0922	1.0939
C1C4	2.9263	2.9088	2.9132	2.9218
C3C4	1.5279	1.5197	1.5215	1.5262
C2C3	1.5296	1.5217	1.5230	1.5282
C4Hq	1.0915	1.0879	1.0887	1.0907
C4Ha	1.0947	1.0908	1.0916	1.0939
C3Ha	1.0950	1.0910	1.0918	1.0941
C3Hq	1.0909	1.0873	1.0881	1.0901
C2Hq	1.0908	1.0872	1.0880	1.0900
FC1C4	150.805	151.005	151.007	150.804
C4C1Ha	102.487	102.516	102.312	102.691
C1C4C3	58.639	58.589	58.588	58.640
C2C3C4	111.018	110.926	110.923	111.021
C1C4Hq	150.962	151.130	151.118	150.974
C1C4Ha	102.062	101.922	101.927	102.058
C4C3Ha	109.143	109.160	109.141	109.161
C4C3Hq	110.588	110.684	110.667	110.605
C3C2Hq	111.187	111.260	111.248	111.198
C3C2Ha	109.956	109.970	109.972	109.954
FC1C4C3	105.214	105.332	105.329	105.217
C2C3C4C1	-28.105	-28.292	-28.263	-28.135
C1C4C3Ha	92.491	92.303	92.321	92.472
C1C4C3Hq	-150.383	-150.574	-150.577	-150.380
C4C3C2Hq	177.744	178.072	178.089	177.727
C4C3C2Ha	-63.243	-62.807	-62.858	-63.192

[a]Estimated according to Eq. 1 (see text).

Table S14. Ab initio structures of axial fluorocyclohexane (distances in Å and angles in degree).

Method Basis set	CCSD(T)_AE cc-pwCVTZ	MP2_AE cc-pwCVQZ	MP2_AE cc-pwCVTZ	r_e^{BO}[a]
C1Fa	1.3996	1.4004	1.3987	1.4013
C1Hq	1.0916	1.0884	1.0892	1.0908
C2Ha	1.0944	1.0906	1.0913	1.0937
C2Hq	1.0910	1.0875	1.0883	1.0902
C1C4	2.9378	2.9226	2.9249	2.9355
C3C4	1.5279	1.5197	1.5214	1.5261
C2C3	1.5282	1.5197	1.5214	1.5265
C3Ha	1.0927	1.0889	1.0896	1.0919
C3Hq	1.0912	1.0876	1.0884	1.0905
C4Ha	1.0957	1.0918	1.0925	1.0949
C4Hq	1.0915	1.0879	1.0887	1.0907
FC1C4	102.305	102.591	102.288	102.608
C4C1Ha	151.350	151.301	151.406	151.246
C1C4C3	58.994	58.982	58.949	59.026
C2C3C4	110.966	110.865	110.867	110.964
C1C4Ha	100.716	100.358	100.540	100.534
C1C4Hq	152.406	152.773	152.600	152.579
C4C3Ha	109.290	109.280	109.292	109.279
C4C3Hq	110.568	110.673	110.651	110.590
C3C2Hq	111.039	111.181	111.114	111.107
C3C2Ha	109.878	109.863	109.901	109.839
FC1C4C3	-73.851	-73.591	-73.707	-73.734
C2C3C4C1	-27.273	-27.335	-27.426	-27.183
C1C4C3Ha	92.956	92.924	92.777	93.103
C1C4C3Hq	-149.390	-149.459	-149.593	-149.256
C4C3C2Hq	176.580	176.944	176.943	176.581
C4C3C2Ha	-64.772	-64.435	-64.423	-64.784

[a]Estimated according to Eq. 1 (see text).

Table S15. Values for dihedral angles (in degree) of selected molecules.

molecule	angle	τ_e	MP2 cc-pVTZ	B3LYP 6-311+G	Ref. for τ_e
propane	HaCCC	59.66	59.63	59.81	a
propene	HaCCC	120.57	120.58	120.8192	b
propionitrile	HaCCC	60.06	60.16	60.18	c
methyl formate	HaCOC	60.26	60.31	60.36	d
acetaldehyde	HaCCO	121.49	121.52	121.80	a
dimethylsulfide	HaCSC	61.06	61.09	61.30	e
cyclohexane	HaxCCHax	175.36	175.84	173.20	f
	HaxCCHeq	58.29	58.71	56.64	
	HeqCCC	178.51	178.86	177.28	
	HaxCCC	64.42	64.01	66.16	
	CCCC	55.80	56.14	54.48	
dimethylsulfoxide	CSCHII	-58.43	-58.39	-58.39	g
	CSCHIII	63.47	63.76	63.76	
	CSCHI	-177.11	-176.76	-177.25	
piperidine	C3C4C5C6	53.48	53.78	52.35	f
	HqC4C3Hx	-56.85	-57.36	-55.40	
	HqC4C3Hq	61.90	61.53	62.79	
	HxC4C3C2	66.34	65.95	67.91	
	HqC4C3C2	-176.36	-176.70	-175.26	
	HxC4C3Hx	-174.15	-174.71	-172.23	
	HxC4C3Hq	-55.41	-55.82	-54.03	
	HxC3C4C5	66.02	65.56	67.51	
	HqC3C4C5	-175.23	-175.55	-174.30	
	C4C3C2N	57.46	57.97	55.94	
	HxC2C3C4	-65.01	-64.62	-67.13	
	HqC2C3C4	177.02	177.41	175.53	
	HxC3C2N	-62.71	-62.10	-64.52	
	HqC3C2N	179.97	179.84	178.32	
	HxC3C2Hx	174.82	175.31	172.41	
	HxC3C2Hq	56.84	57.34	55.07	
	HqC3C2Hx	56.91	57.57	55.25	
	HqC3C2Hq	-60.80	-60.40	-62.09	
	C3C2NC6	-63.01	-63.68	-61.54	
	HNC2C3	175.47	175.54	174.80	
	HxC2NH	-64.00	-63.93	-64.17	
	HqC2NH	54.75	54.95	54.10	
	HxC2NC6	57.53	56.85	59.49	
	HqC2NC6	176.27	175.73	177.77	
proline	C6C2N1H9	-118.36	-119.91	-113.08	h
	N1C2C6O8	2.37	2.29	0.71	
	C2C6O8H11	-0.76	-0.16	-0.75	
	N1C2C6O7	-177.59	-177.27	-179.53	

	H9N1C2H10	-0.1	-1.38	4.7	
	H9N1C2C3	122.02	121.02	125.77	
	N1C2C3H12	-90.73	-89.06	-94.32	
	N1C2C3H13	148.97	150.21	146.08	
	N1C2C3C4	25.96	27.46	22.96	
	C2C3C4H14	-161.25	-162.66	-158.44	
	C2C3C4H14	77	75.41	80.59	
	C2C3C4C5	-39.93	-41.43	-37.02	
	C3C4C5H16	-79.69	-78.72	-81.89	
	C3C4C5H17	158.91	159.78	157.16	
deoxyribose	O6C1C2C3	-51.26	-52.79	-50.33	i
	O6C1C2H10	-174.10	-175.42	-173.19	
	O6C1C2H19	68.62	66.99	69.99	
	O16C1C2C3	71.38	69.98	72.87	
	O16C1C2H10	-51.46	-52.65	-49.98	
	O16C1C2H19	-168.74	-170.23	-166.80	
	H18C1C2C3	-166.92	-168.28	-165.77	
	H18C1C2C10	70.23	69.09	71.38	
	H18C1C2H19	-47.05	-48.49	-45.44	
	C2C1O6C5	58.45	59.23	56.83	
	O16C1O6C5	-62.07	-61.15	-64.49	
	H18C1O6C5	178.46	179.31	176.57	
	C2C1O16H17	175.96	175.91	175.38	
	O6C1O16H17	-61.33	-61.32	-61.27	
	H18C1O16H17	54.01	53.89	53.67	
	C1C2C3C4	49.05	50.20	48.83	
	C1C2C3O7	171.97	172.64	172.59	
	C1C2C3H11	-69.64	-69.39	-70.23	
	H10C2C3C4	171.73	172.60	171.51	
	H10C2C3O7	-65.34	-64.96	-64.74	
	H10C2C3H11	52.36	53.00	52.44	
	H19C2C3C4	-70.53	-69.38	-70.99	
	H19C2C3O7	52.40	53.06	52.76	
	H19C2C3H11	170.10	171.02	169.94	
	C2C3C4C5	-52.77	-53.71	-52.23	
	C2C3C4O8	69.31	68.32	71.16	
	C2C3C4H12	-174.18	-175.37	-173.02	
	O7C2C4C5	-176.03	-176.62	-176.28	
	O7C3C4O8	-53.95	-54.59	-52.88	
	O7C3C4H12	62.56	61.72	62.94	
	H11C3C4C5	67.25	66.38	67.52	
	H11C3C4O8	-170.67	-171.59	-169.08	
	H11C3C4H12	-54.16	-55.28	-53.27	
	C2C3O7H9	-79.40	-78.36	-80.63	
	C4C3O7H9	43.25	43.52	42.73	
	H11C3O7H9	161.13	161.88	160.23	
	C3C4C5O6	59.36	59.88	57.84	
	C3C4C5H13	176.03	176.28	174.87	
	C3C4C5H14	-62.75	-62.35	-64.55	
	O8C4C5O6	-62.01	-61.34	-64.74	

O8C4C5H13	54.65	55.07	52.29
O8C4C5H14	175.88	176.43	172.87
H12C4C5O6	-179.78	-179.09	-178.21
H12C4C5H13	-63.12	-62.68	-64.76
H12C4C5H14	58.11	58.68	55.82
C3C4O8H15	-85.59	-86.16	-86.07
C5C4O8H15	35.77	35.32	36.39
H12C4O8H15	155.96	155.58	155.94
C4C5O6C1	-62.97	-62.90	-61.12
H13C5O6C1	177.36	177.61	178.83
H14C5O6C1	59.00	59.24	61.10

[a] CCSD(T)_AE/cc-pwCVQZ value. [b] J. Demaison and H. D. Rudolph, *J. Mol. Spectrosc.,* 2008, **248**, 66-76. [c] J. Demaison, L. Margulès, H. Mäder, M. Sheng and H. D. Rudolph, *J. Mol. Spectrosc.,* 2008, **252**, 169-175. [d] J. Demaison, L. Margulès, I. Kleiner and A. G. Császár, *J. Mol. Spectrosc.,* 2010, **259**, 70-79. [e] J. Demaison, L. Margulès and H. D. Rudolph, *J. Mol. Struct.,* 2010, **978**, 229-233. [f] J. Demaison, N. C. Craig, P. Groner, P. Écija, E. J. Cocinero, A. Lesarri and H. D. Rudolph, *J. Phys. Chem. A* 2015, **119**, 1486-1493. [g] N. Vogt, J. Demaison and H. D. Rudolph, *J. Mol. Spectrosc.,* 2014, **297**, 11-15. [h] N. Vogt, J. Demaison, S. V. Krasnoshchkov, N. F. Stepanov and H. D. Rudolph, *Mol. Phys.,* 2017, **115**, 942-951. [i] N. Vogt, J. Demaison, E. J. Cocinero, P. Écija, A. Lesarri, H. D. Rudolph and J. Vogt, *Phys. Chem. Chem. Phys.,* 2016, **18**, 15555-15563.

Table S16. Calculation of the predicate of the torsional angle for both conformers of fluorocyclohexane and for cyclohexanone (in degree).

	MP2 cc-pVTZ	B3LYP 6-311+ [a]	τ_e [b]	predicate	τ_e – pred.
Equatorial fluorocyclohexane					
C1C2C3C4	56.36	54.76	55.97	55.89	0.08
FqC1C2C3	-178.55	-177.38	-178.18	-178.20	0.02
FqC1C2Hq	58.71	59.88	59.11	59.06	0.05
FqC1C2Ha	-58.33	-56.78	-57.93	-57.87	-0.06
C1C2C3Hq	179.07	177.48	178.64	178.60	0.04
C1C2C3Ha	-64.05	-66.24	-64.53	-64.70	0.17
C2C3C4Hq	-178.51	-176.9	-178.2	-178.03	-0.17
C2C3C4Ha	64.18	66.39	64.58	64.83	-0.25
Axial fluorocyclohexane					
C1C2C3C4	55.2	53.25	54.66	54.62	0.04
C3C2C1Hq	-178.14	-176.3	-177.57	-177.59	0.02
HqC1C2Hq	58.88	60.31	59.31	59.30	0.01
HqC1C2Ha	-57.44	-55.25	-56.89	-56.79	-0.10
C1C2C3Hq	177.79	175.92	177.2	177.24	-0.04
C1C2C3Ha	-65.13	-67.59	-65.76	-65.86	0.10
C2C3C4Hq	-179.36	-177.64	-179.07	-178.85	-0.22
C2C3C4Ha	63.36	65.68	63.73	64.05	-0.32
Cyclohexanone					
C1C2C3C4	54.38	51.62	53.46	53.56	-0.10
C2C3C4C5	-57.56	-56.05	-57.37	-57.11	-0.26
C6C1C2C3	-53.51	-48.68	-51.63	-52.08	0.45
OC1C2C3	124.37	131.22	127.19	126.40	0.79
OC1C2Hq	0.97	6.88	3.43	2.72	0.71
OC1C2Ha	-116.75	-109.29	-113.79	-114.54	0.75
C1C2C3Hq	177.17	174.55	176.24	176.40	-0.16
C1C2C3Ha	-66.00	-69.29	-67	-66.98	-0.02
C2C3C4Hq	-179.71	-178.22	-179.48	-179.27	-0.21
C2C3C4Ha	63.03	65.06	63.28	63.63	-0.35
MAD [c]					0.10
σ [d]					0.31

[a] 6-311+G(3df,2pd). [b] See Tables 3, 4, and 5. [c] Median absolute deviation. [d] Standard deviation.

Table S17. Rovibrational corrections X_e - X_0, semiexperimental equilibrium rotational constants X_e^{SE}, residuals of the fit (all values in MHz) and leverage values h_{ii} for equatorial fluorocyclohexane.

Isotopologue	Axis	X_e - X_0	X_e^{SE}	exp - calc	h_{ii}
Parent	*a*	47.413	4360.784	-0.001	0.62
	b	19.063	2207.866	0.000	0.67
	c	14.988	1606.609	0.006	0.35
^{13}C1	*a*	47.162	4356.759	-0.001	0.89
	b	18.869	2198.585	0.001	0.83
	c	14.847	1602.225	-0.001	0.44
^{13}C2	*a*	46.480	4301.633	-0.002	0.95
	b	18.955	2206.918	-0.001	0.71
	c	14.839	1598.334	-0.001	0.49
^{13}C3	*a*	46.500	4301.581	0.001	0.94
	b	18.819	2192.997	0.002	0.83
	c	14.755	1591.131	-0.006	0.47
^{13}C4	*a*	47.189	4357.770	0.002	0.88
	b	18.699	2172.085	-0.002	0.84
	c	14.743	1587.977	0.003	0.44

[a] *X* = *A, B, C*

Table S18. Rovibrational corrections X_e - X_0, semiexperimental equilibrium rotational constants X_e^{SE}, residuals of the fit (all values in MHz) and leverage values h_{ii} for axial fluorocyclohexane.

Isotopologue	Axis	X_e - X_0	X_e^{SE}	exp - calc	h_{ii}
Parent	*a*	31.318	3594.287	0.029	0.24
	b	30.265	2658.890	-0.025	0.43
	c	24.505	2005.387	0.005	0.31
^{13}C1	*a*	30.948	3588.092	-0.063	0.38
	b	29.986	2639.733	0.007	0.74
	c	24.324	1996.345	0.014	0.42
^{13}C2	*a*	30.641	3544.399	-0.048	0.57
	b	30.097	2652.672	0.041	0.45
	c	24.255	1992.365	0.017	0.43
^{13}C3	*a*	30.807	3553.010	0.014	0.56
	b	30.031	2644.616	-0.026	0.45
	c	24.153	1985.884	-0.020	0.47
^{13}C4	*a*	31.176	3594.004	0.066	0.25
	b	29.671	2614.475	-0.016	0.62
	c	24.074	1980.090	-0.015	0.45

[a] *X = A, B, C*

Table S19. Cartesian coordinates for the semiexperimental equilibrium structure of equatorial fluorocyclohexane (in Å).

	a_e	b_e	c_e
C1	-0.92971(27)	0	0.32898(37)
C2	-0.25583(69)	1.25371(13)	-0.18171(66)
C3	1.22310(19)	1.25710(11)	0.21498(41)
C4	1.92679(14)	0	-0.28680(51)
C5	1.22310(19)	-1.25710(11)	0.21498(41)
C6	-0.25583(69)	-1.25371(13)	-0.18171(66)
Fq	-2.26104(56)	0	-0.07956(57)
H1a	-0.9403(28)	0	1.4231(14)
H2q	-0.7732(30)	2.1293(17)	0.2085(35)
H2a	-0.3544(61)	1.2709(25)	-1.2706(13)
H3q	1.7090(28)	2.1497(17)	-0.1770(31)
H3a	1.2999(47)	1.3024(25)	1.3060(12)
H4q	2.9704(16)	0	0.0295(29)
H4a	1.9236(27)	0	-1.3809(14)
H5q	1.7090(28)	-2.1497(17)	-0.1770(31)
H5a	1.2999(47)	-1.3024(25)	1.3060(12)
H6q	-0.7732(30)	-2.1293(17)	0.2085(35)
H6a	-0.3544(61)	-1.2709(25)	-1.2706(13)

Table S20. Cartesian coordinates for the semiexperimental equilibrium structure of axial fluorocyclohexane (in Å).

	a_e	b_e	c_e
H1q	-1.8973(22)	0	-1.2055(24)
C1	-1.07120(79)	0	-0.49310(99)
Fa	-1.6563(10)	0	0.78274(90)
C2	-0.2443(12)	1.26071(57)	-0.63367(62)
C6	-0.2443(12)	-1.26071(57)	-0.63367(62)
C3	0.95313(64)	1.25547(57)	0.3118(12)
C5	0.95313(64)	-1.25547(57)	0.3118(12)
C4	1.79931(55)	0	0.1138(17)
H4q	2.6428(37)	0	0.8050(53)
H4a	2.2154(42)	0	-0.8990(34)
H2q	-0.8825(30)	2.1264(21)	-0.4556(43)
H2a	0.0964(65)	1.3179(30)	-1.6715(25)
H6q	-0.8825(30)	-2.1264(21)	-0.4556(43)
H6a	0.0964(65)	-1.3179(30)	-1.6715(25)
H3q	1.5536(27)	2.1509(21)	0.1499(43)
H3a	0.5887(68)	1.2911(30)	1.3407(31)
H5q	1.5536(27)	-2.1509(21)	0.1499(43)
H5a	0.5887(68)	-1.2911(30)	1.3407(31)

Table S21. Comparison of the r_s structure and the semiexperimental equilibrium structure, r_e^{SE}, for equatorial fluorocyclohexane.

Cartesian coordinates[a] (Å)

	a_s	a_e	b_s	b_e	c_s	c_e
C1	-0.927(2)[b](4)[c]	-0.9297(3)	I[d]	0	0.331(5)(10)	0.3290(4)
C2	-0.239(6)(14)	-0.2558(7)	1.258(1)(3)	1.2537(1)	-0.178(8)(19)	-0.1817(7)
C3	1.224(1)(3)	1.2231(2)	1.262(1)(3)	1.2571(1)	0.212(7)(17)	0.2150(4)
C4	1.934(1)(4)	1.9268(1)	I[d]	0	-0.289(5)(29)	-0.2868(5)

Internal coordinates[d] (distances in Å and angles in degree)

	r_s	r_e^{SE}		r_s	r_e^{SE}
C1C2	1.522(4)	1.5122(4)	C1C2C3	110.64(36)	110.17(3)
C2C3	1.514(7)	1.5312(7)	C2C3C4	111.18(29)	111.01(2)
C3C4	1.532(3)	1.5255(3)	C1C2C3C4	55.89(70)	55.99(5)

[a]See Table S19. [b]The uncertainties are given in parentheses. The first digit is calculated with Costain's rule, $\delta z = 0.0015/|z|$. [c]The second parentheses represent the uncertainty calculated taking into account the variation of the rovibrational correction upon isotopic substitution. [d]Imaginary coordinate.