Supplementary Material (ESI) for New Journal of Chemistry

Experimental determination of the conformational free energies (A Values) of fluorinated substituents in cyclohexane by dynamic ^{19}F NMR spectroscopy, Part 1: description of the method for the trifluoromethyl group.

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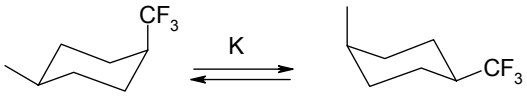
Chemical shifts must be read with one digit after the comma, but all the numbers are required and are given by the software of simulated spectra.

Table 1: ^{19}F NMR chemical shifts (ppm) of 4-methyl-1-trifluoromethylcyclohexane[a]

T / K	*trans* isomer[b]	*cis* isomer		
		δ_{obs} [b]	δ_{ax} [b.c]	δ_{eq} [b.c]
298	**-71.912**	**-70.341**	*-64.402*	*-72.547*
293	**-71.902**	**-70.355**	*-64.366*	*-72.514*
288	**-71.890**	**-70.370**	*-64.329*	*-72.480*
283	**-71.878**	**-70.385**	*-64.293*	*-72.446*
278	**-71.865**	**-70.399**	*-64.256*	*-72.412*
273	**-71.851**	**-70.416**	*-64.220*	*-72.379*
268	**-71.836**	**-70.432**	*-64.183*	*-72.345*
263	**-71.820**	**-70.449**	*-64.146*	*-72.311*
258	**-71.803**	**-70.471**	*-64.110*	*-72.277*
253	**-71.785**	**-70.493**	*-64.073*	*-72.244*
243	**-71.746**	-	-	-
223	**-71.657**	-	-	-
213	**-71.605**	-	-	-
203	**-71.548**	-	**-63.686**	**-71.901**
193	**-71.491**	-	**-63.635**	**-71.839**
188	**-71.460**	-	**-63.600**	**-71.807**
183	**-71.428**	-	**-63.562**	**-71.772**
178	**-71.393**	-	**-63.526**	**-71.738**

[a] Chemical shifts are in ppm and were measured in THF-d^8 relative to $CFCl_3$.
[b] Shifts in bold are experimental values.
[c] Shifts in italic were calculated by linear regression: $\delta_{ax.} = -62.224 - 7.31.10^{-3}\ T$
$\delta_{eq.} = -70.536 - 6.75.10^{-3}\ T$

Table 2: Equilibrium parameters of *cis*-4-methyl-1-trifluoromethylcyclohexane



T / K	K[a]	ΔG° / J.mol^{-1}
298	2.690	-2452
293	2.775	-2486
288	2.863	-2519
283	2.956	-2551
278	3.052	-2579
273	3.157	-2610
268	3.267	-2638
263	3.383	-2665
258	3.520	-2700
253	3.666	-2733

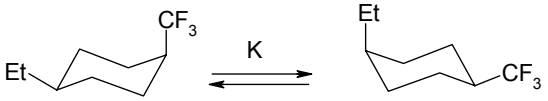
[a] Equilibrium constants were calculated from the values of the chemical shifts: $K = (\delta_{ax} - \delta_{obs}) / (\delta_{obs} - \delta_{eq})$

Table 3: ^{19}F NMR chemical shifts (ppm) of 4-ethyl-1-trifluoromethylcyclohexane[a]

T / K	*trans* isomer[b]	*cis* isomer		
		δ_{obs} [b]	δ_{ax} [b.c]	δ_{eq} [b.c]
298	**-73.746**	**-72.191**	*-66.227*	*-74.392*
293	**-73.735**	**-72.214**	*-66.189*	*-74.358*
288	**-73.724**	**-72.238**	*-66.151*	*-74.323*
283	**-73.712**	**-72.261**	*-66.114*	*-74.288*
278	**-73.699**	**-72.283**	*-66.076*	*-74.254*
273	**-73.686**	**-72.304**	*-66.038*	*-74.219*
268	**-73.671**	**-72.328**	*-66.000*	*-74.184*
263	**-73.656**	**-72.355**	*-65.962*	*-74.150*
258	**-73.639**	**-72.383**	*-65.925*	*-74.115*
253	**-73.622**	**-72.412**	*-65.887*	*-74.080*
248	**-73.603**	**-72.459**	*-65.849*	*-74.046*
228	**-73.515**	-	-	-
208	**-73.411**	-	-	-
198	**-73.353**	-	-	-
188	**-73.290**	-	**-65.396**	**-73.635**
183	**-73.257**	-	**-65.358**	**-73.602**
178	**-73.223**	-	**-65.321**	**-73.567**
173	**-73.187**	-	**-65.282**	**-73.531**
168	**-73.152**	-	**-65.245**	**-73.496**

[a] Chemical shifts are in ppm and were measured in THF-d^8 relative to $CFCl_3$.
[b] Shifts in bold are experimental values.
[c] Shifts in italic were calculated by linear regression: $\delta_{ax.} = -63.974 - 7.56.10^{-3}$ T
$\delta_{eq.} = -72.327 - 6.93.10^{-3}$ T

Table 4: Equilibrium parameters of *cis*-4-ethyl-1-trifluoromethylcyclohexane



T / K	K[a]	ΔG° / J.mol^{-1}
298	2.710	-2470
293	2.811	-2518
288	2.918	-2564
283	3.031	-2609
278	3.149	-2651
273	3.272	-2691
268	3.409	-2732
263	3.562	-2778
258	3.730	-2823
253	3.911	-2869

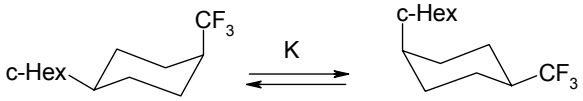
[a] Equilibrium constants were calculated from the values of the chemical shifts: $K = (\delta_{ax} - \delta_{obs}) / (\delta_{obs} - \delta_{eq})$

Table 5: ^{19}F NMR chemical shifts (ppm) of 4-cyclohexyl-1-trifluoromethylcyclohexane[a]

T / K	*trans* isomer[b]	*cis* isomer		
		δ_{obs} [b]	δ_{ax} [b.c]	δ_{eq} [b.c]
298	**-73.788**	**-71.252**	*-66.233*	*-74.304*
293	**-73.778**	**-71.285**	*-66.195*	*-74.273*
288	**-73.768**	**-71.319**	*-66.156*	*-74.242*
283	**-73.756**	**-71.356**	*-66.118*	*-74.211*
278	**-73.744**	**-71.392**	*-66.079*	*-74.180*
273	**-73.731**	**-71.428**	*-66.041*	*-74.149*
268	**-73.717**	**-71.468**	*-66.002*	*-74.118*
263	**-73.702**	**-71.510**	*-65.964*	*-74.087*
258	**-73.686**	**-71.553**	*-65.925*	*-74.056*
253	**-73.669**	**-71.599**	*-65.887*	*-74.025*
238	**-73.613**	-	-	-
223	**-73.546**	-	-	-
208	**-73.470**	-	-	-
198	**-73.413**	-	**-65.452**	**-73.683**
193	**-73.383**	-	**-65.426**	**-73.653**
188	**-73.351**	-	**-65.389**	**-73.624**
183	**-73.321**	-	**-65.349**	**-73.594**
178	**-73.287**	-	**-65.311**	**-73.561**
173	**-73.251**	-	**-65.273**	**-73.527**

[a] Chemical shifts are in ppm and were measured in THF-d^8 relative to $CFCl_3$.
[b] Shifts in bold are experimental values.
[c] Shifts in italic were calculated by linear regression: $\delta_{ax.} = -63.94 - 7.69.10^{-3}\ T$
$\delta_{eq.} = -72.46 - 6.19.10^{-3}\ T$

Table 6: Equilibrium parameters of *cis*-4-cyclohexyl-1-trifluoromethylcyclohexane



T / K	K[a]	ΔG° / J.mol^{-1}
298	1.645	-1233
293	1.704	-1298
288	1.766	-1362
283	1.835	-1428
278	1.906	-1491
273	1.980	-1550
268	2.063	-1613
263	2.152	-1675
258	2.248	-1737
253	2.354	-1801

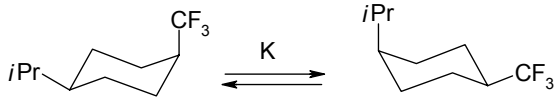
[a] Equilibrium constants were calculated from the values of the chemical shifts: $K = (\delta_{ax} - \delta_{obs}) / (\delta_{obs} - \delta_{eq})$

Table 7: ^{19}F NMR chemical shifts (ppm) of 4-isopropyl-1-trifluoromethylcyclohexane[a]

T / K	*trans* isomer[b]	*cis* isomer		
		δ_{obs} [b]	δ_{ax} [b.c]	δ_{eq} [b.c]
297	**-73.767**	**-71.083**	*-66.371*	*-74.457*
293	**-73.760**	**-71.109**	*-66.336*	*-74.428*
288	**-73.748**	**-71.144**	*-66.293*	*-74.392*
283	**-73.737**	**-71.181**	*-66.249*	*-74.356*
278	**-73.723**	**-71.219**	*-66.206*	*-74.320*
273	**-73.710**	**-71.259**	*-66.162*	*-74.284*
268	**-73.696**	**-71.300**	*-66.119*	*-74.248*
263	**-73.680**	**-71.342**	*-66.075*	*-74.212*
258	**-73.664**	**-71.384**	*-66.032*	*-74.177*
253	**-73.647**	**-71.420**	*-65.988*	*-74.141*
248	**-73.629**	-	-	-
228	**-73.544**	-	-	-
208	**-73.443**	-	-	-
198	**-73.387**	-	-	-
188	**-73.324**	-	**-65.424**	**-73.674**
183	**-73.289**	-	**-65.381**	**-73.640**
178	**-73.251**	-	**-65.337**	**-73.602**
173	**-73.215**	-	**-65.294**	**-73.566**

[a] Chemical shifts are in ppm and were measured in THF-d^8 relative to $CFCl_3$.
[b] Shifts in bold are experimental values.
[c] Shifts in italic were calculated by linear regression: $\delta_{ax.} = -63.79 - 8.69.10^{-3}\ T$
$\delta_{eq.} = -72.32 - 7.18.10^{-3}\ T$

Table 8: Equilibrium parameters of *cis*-4-isopropyl-1-trifluoromethylcyclohexane



T / K	K[a]	ΔG° / J.mol^{-1}
297	1.397	-8256
293	1.438	-885
288	1.493	-960
283	1.554	-1036
278	1.617	-1110
273	1.684	-1183
268	1.758	-1257
263	1.835	-1327
258	1.916	-1395
253	1.996	-1454

[a] Equilibrium constants were calculated from the values of the chemical shifts: $K = (\delta_{ax} - \delta_{obs}) / (\delta_{obs} - \delta_{eq})$

Table 9: ^{19}F NMR chemical shifts (ppm) of 4-*tert*butyl-1-trifluoromethylcyclohexane[a]

T / K	*trans* isomer	*cis* isomer
297	-73.785	-66.396
293	-73.777	-66.360
288	-73.766	-66.315
283	-73.754	-66.278
278	-73.741	-66.229
273	-73.728	-66.186
268	-73.714	-66.145
263	-73.697	-66.100
258	-73.681	-66.058
253	-73.664	-66.016
248	-73.646	-65.973
228	-73.560	-65.806
208	-73.458	-65.643
188	-73.337	-65.481
168	-73.198	-65.314

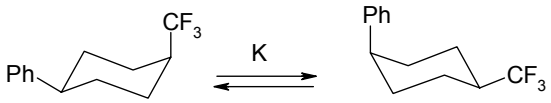
[a] Chemical shifts are in ppm and were measured in THF-d^8 relative to $CFCl_3$.

Table 10: ^{19}F NMR chemical shifts (ppm) of 4-phenyl-1-trifluoromethylcyclohexane[a]

T / K	*trans* isomer[b]	*cis* isomer		
		δ_{obs} [b]	δ_{ax} [b.c]	δ_{eq} [b.c]
298	**-71.832**	**-66.772**	*-64.275*	*-72.489*
293	**-71.823**	**-66.741**	*-64.238*	*-72.459*
288	**-71.813**	**-66.710**	*-64.200*	*-72.429*
283	**-71.802**	**-66.686**	*-64.163*	*-72.399*
278	**-71.791**	**-66.656**	*-64.125*	*-72.369*
273	**-71.779**	**-66.622**	*-64.088*	*-72.339*
268	**-71.768**	**-66.586**	*-64.050*	*-72.309*
263	**-71.753**	**-66.543**	*-64.013*	*-72.279*
258	**-71.739**	-	-	-
253	**-71.723**	-	-	-
233	**-71.648**	-	-	-
213	**-71.556**	-	-	-
203	**-71.503**	-	-	-
198	**-71.479**	-	-	-
193	**-71.460**	-	**-63.488**	-
188	**-71.432**	-	**-63.452**	**-71.829**
183	**-71.402**	-	**-63.415**	**-71.799**
178	**-71.370**	-	**-63.376**	**-71.770**
173	**-71.338**	-	**-63.339**	**-71.739**

[a] Chemical shifts are in ppm and were measured in THF-d^8 relative to $CFCl_3$.
[b] Shifts in bold are experimental values.
[c] Shifts in italic were calculated by linear regression: $\delta_{ax.} = -62.04 - 7.49.10^{-3}$ T
$\delta_{eq.} = -70.70 - 5.99.10^{-3}$ T

Table 11: Equilibrium parameters of *cis*-4-phenyl-1-trifluoromethylcyclohexane



T / K	K[a]	ΔG° / J.mol^{-1}
298	0.437	2053
293	0.438	2011
288	0.439	1972
283	0.442	1923
278	0.443	1883
273	0.443	1846
268	0.443	1814
263	0.441	1790

[a] Equilibrium constants were calculated from the values of the chemical shifts: $K = (\delta_{ax} - \delta_{obs}) / (\delta_{obs} - \delta_{eq})$

Table 12: ^{19}F NMR chemical shifts (ppm) of trifluoromethylcyclohexane[a]

T / K	δ_{obs}
298	-74.055
293	-74.052
288	-74.048
283	-74.043
278	-74.036
273	-74.029
268	-74.021
263	-74.012
258	-74.002
253	-73.988
248	-73.975
228	-73.911
208	-73.834
188	-73.714
168	-73.596

[a] Chemical shifts are in ppm and were measured in THF-d^8 relative to $CFCl_3$.

Table 13: ^{19}F NMR chemical shifts (ppm) of 1,4-bis(trifluoromethyl)-cyclohexane[a]

T / K	*trans* isomer[b]	*cis* isomer		
		δ_{obs} [b]	δ_{ax} [b.c]	δ_{eq} [b.c]
297	-73.819	-70.207	-	-
288	-73.798	-70.174	-	-
278	-73.771	-70.134	-	-
268	-73.741	-70.092	-	-
258	-73.707	-70.047	-	-
248	-73.669	-70.001	-	-
228	-73.579	-	-	-
208	-73.485	-	-	-
188	-73.362	-	-65.655	-73.655
183	-73.330	-	-65.621	-73.617
178	-73.297	-	-65.590	-73.582
173	-73.260	-	-65.553	-73.545

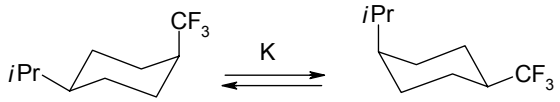
[a] Chemical shifts are in ppm and were measured in THF-d^8 relative to $CFCl_3$.

Table 14: ^{19}F NMR chemical shifts (ppm) of 4-isopropyl-1-trifluoromethylcyclohexane in toluene-d8[a]

T / K	*trans* isomer[b]	*cis* isomer		
		δ_{obs} [b]	δ_{ax} [b.c]	δ_{eq} [b.c]
297	**-78.903**	**-76.272**	*-71.810*	*-79.418*
293	**-78.888**	**-76.296**	*-71.758*	*-79.383*
288	**-78.868**	**-76.329**	*-71.693*	*-79.340*
283	**-78.847**	**-76.361**	*-71.629*	*-79.296*
278	**-78.826**	**-76.395**	*-71.565*	*-79.252*
273	**-78.803**	**-76.431**	*-71.501*	*-79.209*
268	**-78.779**	**-76.465**	*-71.436*	*-79.165*
263	**-78.753**	**-76.502**	*-71.372*	*-79.121*
243	**-78.633**	-	-	-
223	**-78.489**	-	-	-
203	**-78.325**	-	**-70.600**	**-78.597**
193	**-78.235**	-	**-70.462**	**-78.511**
188	**-78.190**	-	**-70.409**	**-78.465**
183	**-78.177**	-	**-70.387**	**-78.452**
178	**-78.174**	-	**-70.380**	**-78.448**

[a] Chemical shifts are in ppm and were measured in toluene-d^8 relative to $CFCl_3$.
[b] Shifts in bold are experimental values.
[c] Shifts in italic were calculated by linear regression: $\delta_{ax.} = -67.982 - 1.289.10^{-2}\ T$
$\delta_{eq.} = -76.823 - 8.73.10^{-3}\ T$

Table 15: Equilibrium parameters of *cis*-4-isopropyl-1-trifluoromethylcyclohexane



T / K	K[a]	ΔG° / J.mol^{-1}
297	1.418	-863
293	1.470	-939
288	1.539	-1033
283	1.612	-1123
278	1.691	-1214
273	1.774	-1302
268	1.862	-1386
263	1.959	-1470

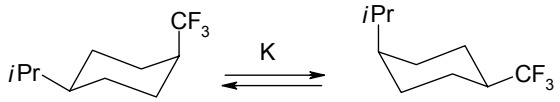
[a] Equilibrium constants were calculated from the values of the chemical shifts: $K = (\delta_{ax} - \delta_{obs}) / (\delta_{obs} - \delta_{eq})$

Table 16: ^{19}F NMR chemical shifts (ppm) of 4-isopropyl-1-trifluoromethylcyclohexane in methanol-d4[a]

T / K	*trans* isomer[b]	*cis* isomer		
		δ_{obs} [b]	δ_{ax} [b.c]	δ_{eq} [b.c]
297	**-71.972**	**-69.172**	*-64.518*	*-72.707*
293	**-71.968**	**-69.225**	*-64.485*	*-72.678*
288	**-71.962**	**-69.277**	*-64.444*	*-72.642*
283	**-71.954**	**-69.329**	*-64.403*	*-72.606*
278	**-71.944**	**-69.383**	*-64.361*	*-72.570*
273	**-71.934**	**-69.434**	*-64.319*	*-72.534*
268	**-71.922**	**-69.487**	*-64.278*	*-72.497*
263	**-71.909**	**-69.539**	*-64.237*	*-72.461*
243	**-71.850**	-	-	-
223	**-71.764**	-	-	-
203	**-71.647**	-	-	**-72.025**
193	**-71.580**	-	**-63.655**	**-71.956**
188	**-71.546**	-	**-63.619**	**-71.920**
183	**-71.509**	-	**-63.573**	**-71.882**
178	**-71.470**	-	**-63.532**	**-71.843**

[a] Chemical shifts are in ppm and were measured in CD_3OD relative to $CFCl_3$.
[b] Shifts in bold are experimental values.
[c] Shifts in italic were calculated by linear regression: $\delta_{ax.} = -62.056 - 8.29.10^{-3}\ T$
$\delta_{eq.} = -70.557 - 7.24.10^{-3}\ T$

Table 17: Equilibrium parameters of *cis*-4-isopropyl-1-trifluoromethylcyclohexane



T / K	K[a]	ΔG° / J.mol^{-1}
297	1.316	-679
293	1.372	-771
288	1.436	-867
283	1.504	-960
278	1.576	-1051
273	1.650	-1137
268	1.730	-1221
263	1.814	-1302

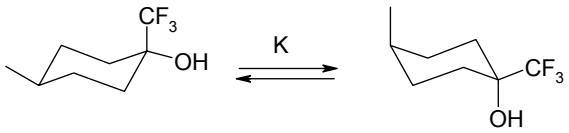
[a] Equilibrium constants were calculated from the values of the chemical shifts: $K = (\delta_{ax} - \delta_{obs}) / (\delta_{obs} - \delta_{eq})$

Table 18: ^{19}F NMR chemical shifts (ppm) of 4-methyl-1-trifluoromethylcyclohexanol[a]

T / K	*cis* isomer[b]	*trans* isomer		
		δ_{obs} [b]	δ_{ax} [b.c]	δ_{eq} [b.c]
298	**-84.560**	**-83.111**	*-77.228*	*-85.300*
293	**-84.555**	**-83.140**	*-77.206*	*-85.275*
288	**-84.550**	**-83.169**	*-77.184*	*-85.250*
283	**-84.545**	**-83.199**	*-77.162*	*-85.225*
278	**-84.540**	**-83.228**	*-77.140*	*-85.201*
273	**-84.533**	**-83.257**	*-77.118*	*-85.176*
268	**-84.526**	**-83.287**	*-77.096*	*-85.151*
263	**-84.519**	**-83.319**	*-77.074*	*-85.126*
258	**-84.510**	**-83.355**	*-77.052*	*-85.102*
253	**-84.500**	**-83.403**	*-77.029*	*-85.077*
248	**-84.491**	-	-	-
243	**-84.480**	-	-	-
238	**-84.467**	-	-	-
233	**-84.454**	-	-	-
228	**-84.439**	-	-	-
218	**-84.408**	-	-	-
208	**-84.373**	-	-	-
203	**-84.354**	-	-	-
198	**-84.335**	-	-	-
193	**-84.314**	-	-	**-84.780**
188	**-84.292**	-	**-76.742**	**-84.756**
183	**-84.269**	-	**-76.718**	**-84.733**
178	**-84.245**	-	**-76.698**	**-84.707**
173	**-84.220**	-	**-76.675**	**-84.681**
168	**-84.208**	-	**-76.653**	**-84.657**

[a] Chemical shifts are in ppm and were measured in THF-d^8 relative to $CFCl_3$.
[b] Shifts in bold are experimental values.
[c] Shifts in italic were calculated by linear regression: $\delta_{ax.} = -75.911 - 4.42.10^{-3}\ T$
$\delta_{eq.} = -83.825 - 4.95.10^{-3}\ T$

Table 19: Equilibrium parameters of *trans*-4-methyl-1-trifluoromethylcyclohexanol[a]



T / K	K[a]	ΔG° / J.mol^{-1}
298	2.688	-2450
293	2.779	-2490
288	2.875	-2529
283	2.978	-2568
278	3.0859	-2604
273	3.198	-2639
268	3.321	-2674
263	3.456	-2711
258	3.607	-2752
253	3.806	-2812

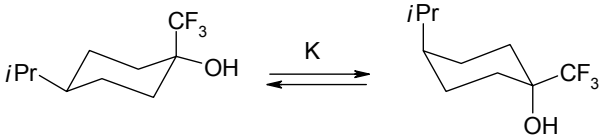
[a] K were calculated from the values of the chemical shifts: $K = (\delta_{ax} - \delta_{obs}) / (\delta_{obs} - \delta_{eq})$

Table 20: ^{19}F NMR chemical shifts (ppm) of 4-isopropyl-1-trifluoromethylcyclohexanol[a]

T / K	*cis* isomer[b]	*trans* isomer		
		δ_{obs} [b]	δ_{ax} [b,c]	δ_{eq} [b,c]
293	**-86.413**	**-83.984**	*-79.089*	*-87.123*
288	**-86.408**	**-84.038**	*-79.064*	*-87.100*
283	**-86.402**	**-84.094**	*-79.038*	*-87.076*
278	**-86.396**	**-84.151**	*-79.013*	*-87.052*
273	**-86.388**	**-84.208**	*-78.987*	*-87.0277*
268	**-86.380**	**-84.268**	*-78.962*	*-87.004*
263	**-86.371**	**-84.330**	*-78.936*	*-86.980*
258	**-86.362**	**-84.391**	*-78.911*	*-86.956*
253	**-86.352**	**-84.458**	*-78.885*	*-86.932*
248	**-86.340**	**-84.523**	*-78.859*	*-86.908*
243	**-86.328**	-	-	-
238	**-86.315**	-	-	-
233	**-86.301**	-	-	-
228	**-86.286**	-	-	-
218	**-86.251**	-	-	-
208	**-86.214**	-	-	-
198	**-86.172**	-	-	-
193	**-86.150**	-	**-**	**-86.620**
188	**-86.125**	-	**-78.5281**	**-86.598**
183	**-86.100**	-	**-78.5014**	**-86.574**
178	**-86.074**	-	**-78.4746**	**-86.550**
173	**-86.047**	-	**-78.4515**	**-86.526**
168	**-86.022**	-	**-78.4253**	**-86.500**

[a] Chemical shifts are in ppm and were measured in THF-d^8 relative to $CFCl_3$.
[b] Shifts in bold are experimental values.
[c] Shifts in italic were calculated by linear regression: $\delta_{ax.} = -77.567 - 5.11.10^{-3}$ T
$\delta_{eq.} = -85.696 - 4.79.10^{-3}$ T

Table 21: Equilibrium parameters of *trans*-4-isopropyl-1-trifluoromethylcyclo-hexanol[a]



T / K	K[a]	ΔG° / J.mol^{-1}
293	1.579	-1114
288	1.646	-1194
283	1.718	-1273
278	1.795	-1352
273	1.877	-1429
268	1.9667	-1507
263	2.064	-1584
258	2.167	-1658
253	2.285	-1738
248	2.409	-1813

[a] Equilibrium constants were calculated from the values of the chemical shifts: $K = (\delta_{ax} - \delta_{obs}) / (\delta_{obs} - \delta_{eq})$