Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

The perfluorinated alcohols *c*$C_6F_{11}OH$, *c*$C_6F_{10}(OH)_2$ and *c*$C_6F_{10}(CF_3)OH$

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1. [N(CH_3)$_4$][$C_7F_{13}O$]

1.1 Synthesis

The synthesis was done in a glass Schlenk flask with Argon as inert gas. Tetramethylammoniumfluoride ($N(CH_3)_3F$) ([TMA]F) (1.40 g, 15 mmol, 1.0 eq.) was dissolved in an excess dimethoxyethane (DME) (40 mL) at −30 °C. Subsequently decafluorocyclohexanon ($C_6F_{10}O$) (**3**) (2.5 mL, 4.17 mg, 15 mmol, 1.0 eq) and trifluoromethyl-trimethylsilane ($(CH_3)_3SiCF_3$) (2.5 mL, 2.1 g, 15 mmol, 1.0 eq) were condensed onto the solution at −30 °C. The solution was warmed to ambient temperature and was stirred for 15 h. After removing all volatile components with dynamic vacuum and recrystallization from dichloromethane (CH_2Cl_2), the ammonium alkoxide was obtained as colourless block-shaped crystals in 42% (2.51 g, 5.96 mmol) yield.

1.2 Analysis with vibrational spectroscopy

As vibrational analysis IR and Raman spectroscopy was done in pure substance at *298 K.* The experimental data are shown in Figure 1-1 and the assignment was done in Table 1-1. The theoretical values were calculated using DFT at the BP86[1, 2]/SV(P)[3]-level of theory with Turbomole[4, 5]. In addition, the module AORORCE[6, 7] was used to calculate the frequencies in the analytic mode.

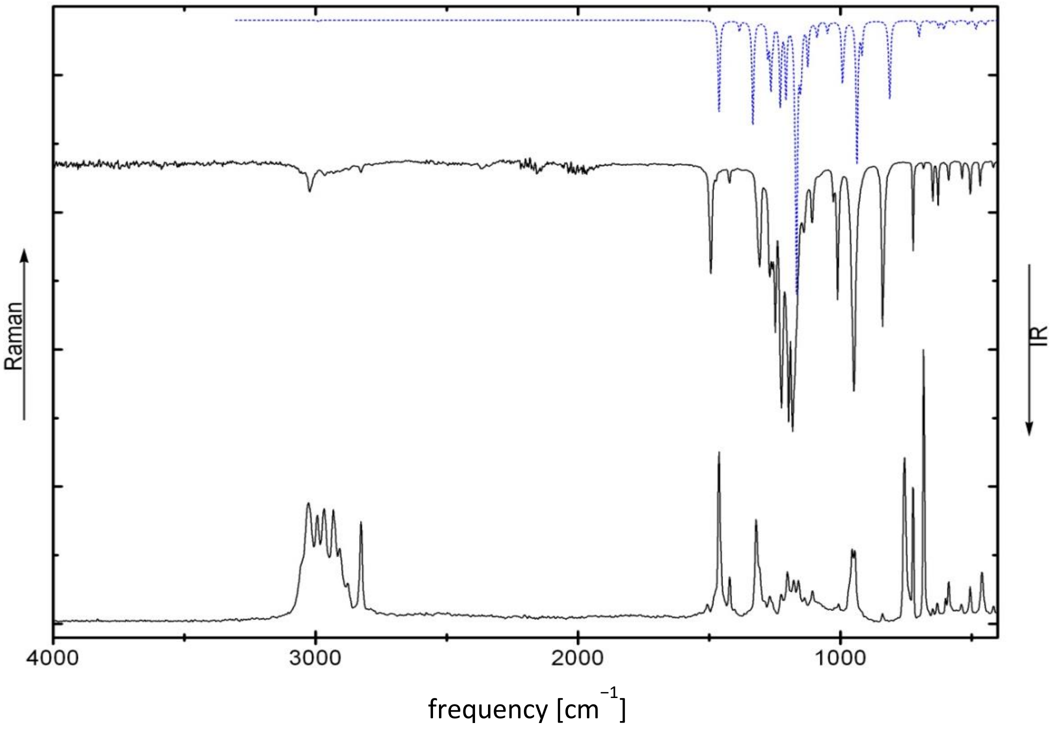


Figure 1-1: IR (top black) and Raman (bottom black) spectra of [N(CH$_3$)$_4$]$^+$[C$_7$F$_{13}$O]$^-$ are compared to the calculated spectra of the anion C$_7$F$_{13}$O$^-$ (dotted blue). The calculated spectrum is shown as Lorenz lines with 10 cm^{-1} line broadening.

Table 1-2:

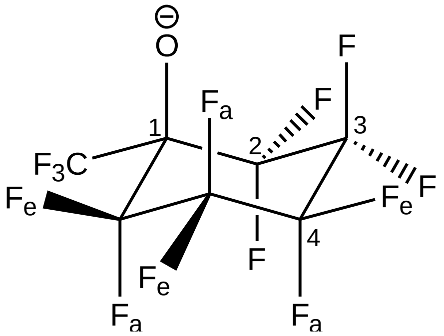
IR (exp.)	**Raman** (exp.)	**Me_4N^+** (cal.)[a)]	**$OC_7F_{13}^-$** (cal.)[a)]	**assignment**
3022 (mw)	3027 (ms)	2992 (vw)	-	C-H
-	2994 (ms)	-	-	-
-	2967 (ms)	-	-	-
-	2932 (ms)	-	-	-
-	2907 (m)	-	-	-
-	2877 (mw)	-	-	-
2827 (vw)	2826 (ms)	-	-	-
-	1507 (w)	-	-	-
1493 (ms)	1462 (s)	1463 (vs)	-	C-H
1422 (w)	1422 (mw)	1385 (mw)	-	C-H
1308 (ms)	1322 (ms)	-	1335 (ms)	C-O, C-C
1269 (s)	1289 (w)	-	1277 (mw)	C-F, C-C
1259 (ms)	1269 (w)	-	1266 (m)	C-C, C-F
1248 (s)	-	-	-	-
1224 (vs)	1225 (w)	-	1228 (m)	C-C, C-F
1197 (vs)	1202 (mw)	-	1206 (m)	C-C, C-F
1182 (vs)	1177 (mw)	-	1167 (vs)	C-F, C-C
-	1159 (mw)	-	1153 (m)	C-F, C-C
1139 (mw)	1136 (w)	-	1125 (mw)	C-F, C-C, C-O
1108 (mw)	1105 (w)	-	1088 (w)	C-C, C-F, C-O
-	-	-	1049 (w)	C-C, C-F
1027 (mw)	-	-	1030 (vw)	C-C, C-F
1010 (ms)	1007 (w)	-	993 (m)	C-F, C-C, C-O
948 (vs)	955 (m)	-	936 (ms)	C-F, C-C
-	945 (m)	918 (m)	-	C-H, C-N
839 (s)	839 (vw)	-	812 (m)	C-F, C-C, C-O
-	754 (s)	-	-	-
723 (m)	724 (ms)	-	700 (w)	C-F, C-C, C-O
683 (vw)	683 (vs)	-	-	C-F, C-C, C-O
648 (w)	648 (vw)	-	655 (vw)	C-F, C-C
628 (w)	631 (w)	-	625 (vw)	C-F, C-C
-	598 (w)	-	605 (vw)	C-F, C-C
588 (vw)	587 (mw)	-	561 (vw)	C-F, C-C
536 (vw)	538 (w)	-	513 (vw)	C-F, C-C
505 (w)	506 (mw)	-	484 (vw)	C-F, C-C
468 (w)	461 (mw)	-	448 (vw)	C-F, C-C

a) The broadening of the spectra was simulated by displaying the calculated vibrations as Lorenz lines with 10 cm^{-1} widths.

1.3 Analysis with NMR-spectroscopy

The NMR spectra were measured at 298 K in deutero-dichloromethane (CD_2Cl_2). ^{19}F-shifts are given with respect to $CFCl_3$, ^{1}H and ^{13}C shifts with respect to TMS. The shifts are listed and assigned in Table 1-3. In the following also the measured NMR spectra are shown (Figure 1-2 to Figure 1-5). Individual coupling constants cannot be directly measured from line distances in the spectrum, because the spin system is an AA'BB'CC'DD'EFG$_3$ and therefore of higher order. The big doublet splitting of the ^{19}F signals of the CF_2-groups for example result from a sum of more than one coupling constant, which is dominated by the $^{2}J_{F\text{-}F}$ coupling.

Table 1-3: NMR-shifts of $[N(CH_3)_4]^+[C_7F_{13}O]^-$ in CD_2Cl_2 at 298 K. Assignments according to the figure shown on the right.

	shift [ppm]	**multiplicity**	**assignment**	**Lewis structure of the anion $C_7F_{13}O^-$ with atom numbering**
δ^{19}F	-73,1	m	CF_3	
	-116,5	m	2a, 3a	
	-122,7	m	4a	
	-135,1	m	2e	
	-138,8	m	3e	
	-142,2	m	4e	
δ^{1}H	3,3	t	CH_3	
δ^{13}C	84.3		1	
	114,1		2	
	109,5		3	
	108,5		4	
	124.6		CF_3	

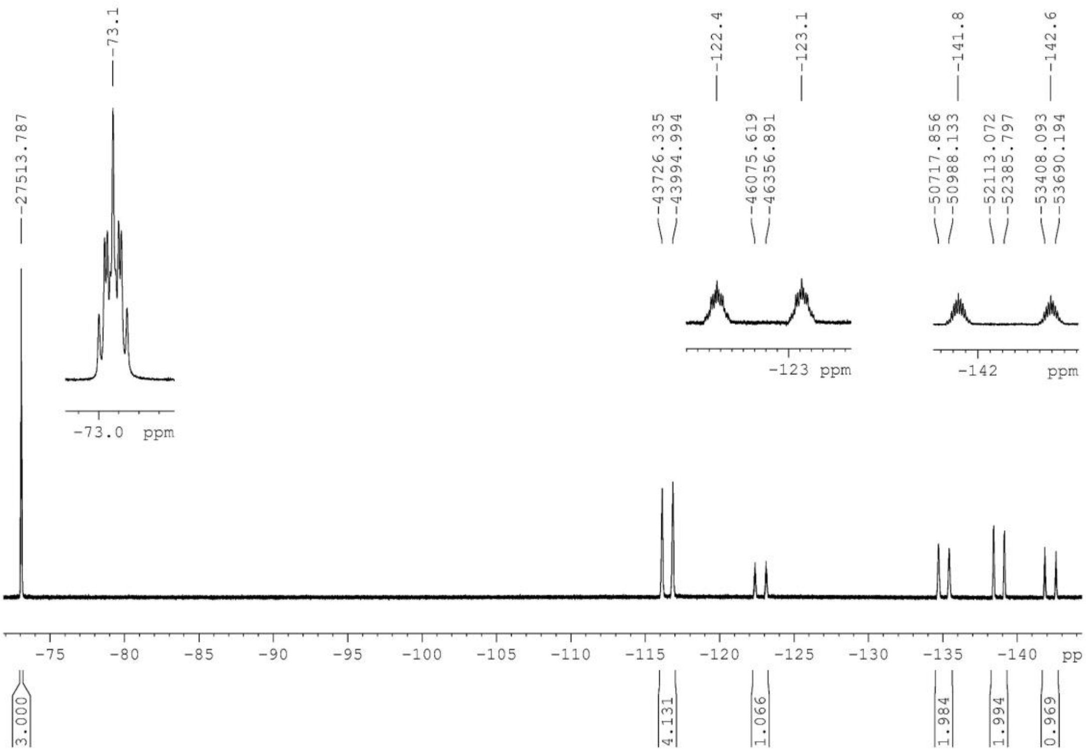


Figure 1-2: ^{19}F-NMR spectrum (376.54 MHz) of $[N(CH_3)_4]^+[C_7F_{13}O]^-$ in CD_2Cl_2 at 298 K. Chemical shifts in ppm.

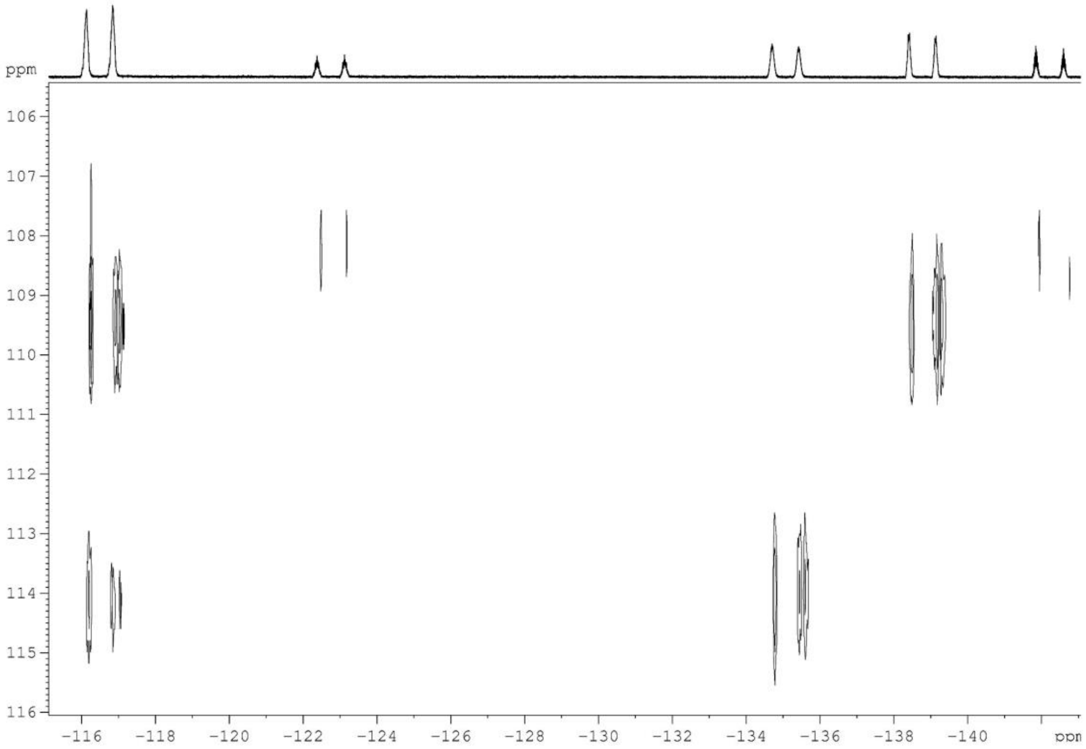


Figure 1-3: ^{19}F,^{13}C HSQC NMR spectrum (376.54 MHz, optimized for $^{1}J_{F\text{-}C}$-couplings) of $[N(CH_3)_4]^+[C_7F_{13}O]^-$ in CD_2Cl_2 at 298 K. (^{19}F plotted horizontal and ^{13}C vertical).

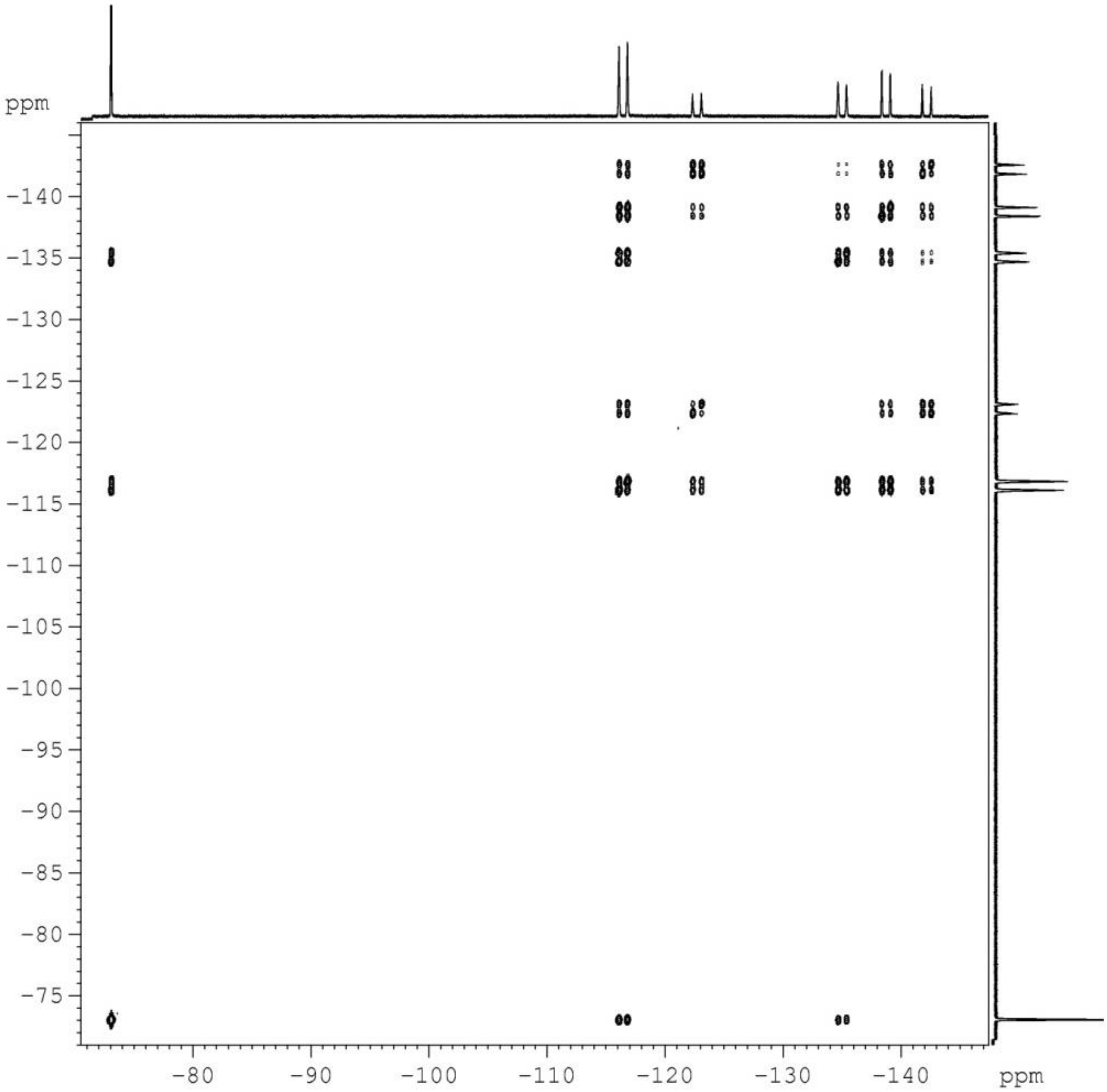


Figure 1-4: ^{19}F COSY NMR spectrum (376.54 MHz) of $[N(CH_3)_4]^+[C_7F_{13}O]^-$ in CD_2Cl_2 at 298 K.

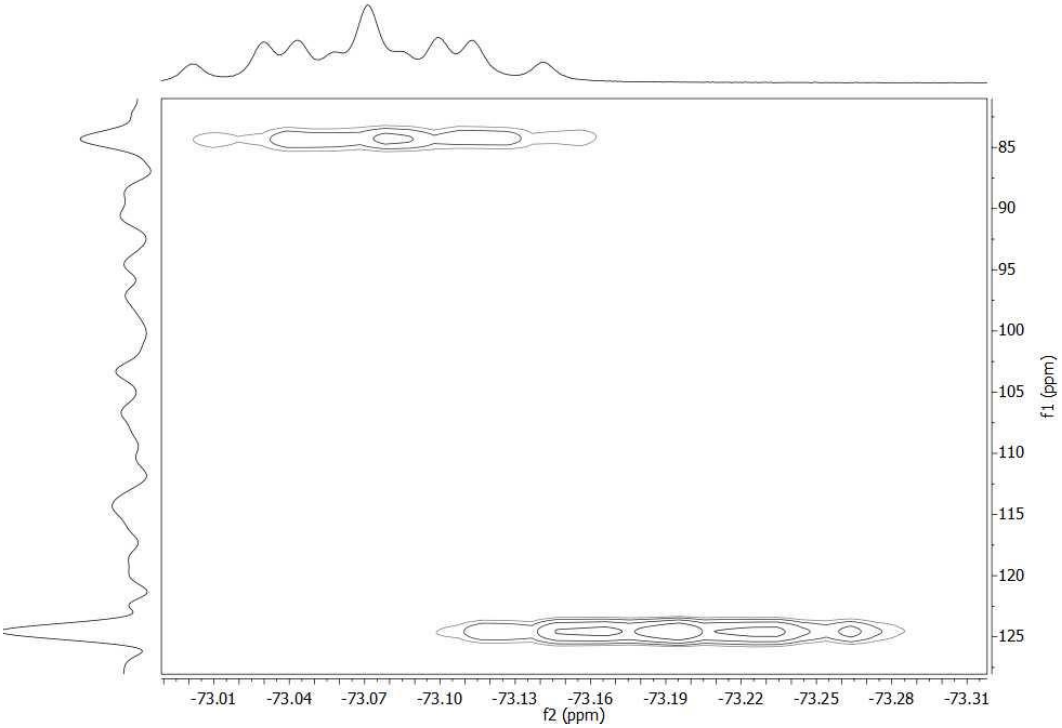


Figure 1-5: Selected area from the $^{19}F,^{13}C$ HSQC NMR spectrum (376.54 MHz, optimized for coupling constants of 60 Hz) of $[N(CH_3)_4]^+[C_7F_{13}O]^-$ in CD_2Cl_2 at 298 K. The crosspeak to the ^{13}C resonance at 124.6 ppm results from a ^1J correlation (^{19}F spectra plotted horizontal and ^{13}C spectra vertical).

1.4 Single crystal X-ray diffraction analysis

The crystals of $[N(CH_3)_4]^+[C_7F_{13}O]^-$ were obtained by recrystallization in CH_2Cl_2. In the following the crystal data and structure refinement parameters are shown in Table 1-4, the asymmetric unit in Figure 1-6 as well as the unit cell along direction a (Figure 1-7), b (Figure 1-8) and c (Figure 1-9).

***Table 1-4**: Crystal data and structure refinement parameters for $[N(CH_3)_4]^+[C_7F_{13}O]^-$*

compound	**$NMe_4^+C_7F_{13}O^-$**	
CCDC	1839041	
Empirical formula	$C_{11}H_{12}F_{13}NO$	
Formula weight	421.22	
Temperature/K	100	
Crystal system	orthorhombic	
Space group	Pnna	
a/Å	14.4972(6)	
b/Å	14.7800(5)	b/Å
c/Å	28.496(2)	c/Å
α/°	90	α/°
β/°	90	
γ/°	90	
Volume/Å^3	6105.8(5)	
Z	16	
ρ_{calc}g/cm^3	1.833	
μ/mm^{-1}	0.224	
F(000)	3360.0	
Crystal size/mm^3	0.29 × 0.25 × 0.22	

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.21 to 54.94
Index ranges	$-18 \le h \le 18$, $-19 \le k \le 19$, $-36 \le l \le 36$
Reflections collected	95237
Independent reflections	6993 [R_{int} = 0.1074, R_{sigma} = 0.0453]
Data/restraints/parameters	6993/0/479
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0459, wR_2 = 0.1041
Final R indexes [all data]	R_1 = 0.0847, wR_2 = 0.1191
Largest diff. peak/hole / e $Å^{-3}$	0.24/-0.33

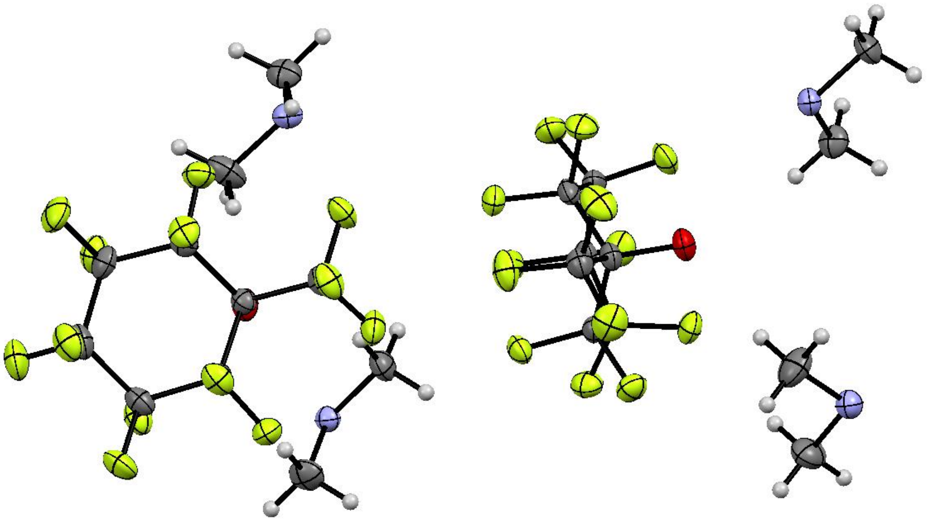


Figure 1-6: Asymmetric unit of $[N(CH_3)_4]^+[C_7F_{13}O]^-$ with two formula units

The C-C bonds are in a range of 1.530(3) (C3-C4) and 1.572(3) Å (C8-C13), which is rather long for a C-C singe bond. The previously published perfluoro-alkylalcohol $(F_5C_6)(F_{10}C_5)COH$ is with an average aliphatic C-C-bond length of 1.556(5) Å in the same range.[8] Also heptafluorocyclobutanol, another perfluoro-alkylalcohol is showing C-C-bond lengths in in the same range.[9]

The C-O bonds are 1.328(3) Å and is significantly shorter than a typical C-O single bond. Instead it is more in the magnitude of a C=O double bond. The C-F bonds are ranging from 1.338(3) (C7-F11) till 1.367(2) (C6-F9), which is in a normal range for perfluoro-alkylalcohols.[8, 9] All C-C-C-angles are in between 106.3(3) (C9-C8-C13) and 114.2(2) Å (C3-C4-C5). The F-C-F angle are ranging from 105.8(2) (F10-C6-F9) to 108.0(2)° (F19-C11-F18). The CCF-angles are in a range of 106.0(2) (F1-C2-C3) and 116.7(2)° (F25-C14-C8). The CCO angle is 110.5(2)° and 110.6(2)°. All observed angles are similar to literature values.[8, 9]

The anions are connected via intermolecular hydrogen bonding from fluorine to the Carbons of the cations. Each cation is bonded to different anions and vice versa. The chair conformation of the anion is more stable, because of the sterically demanding CF_3-group.

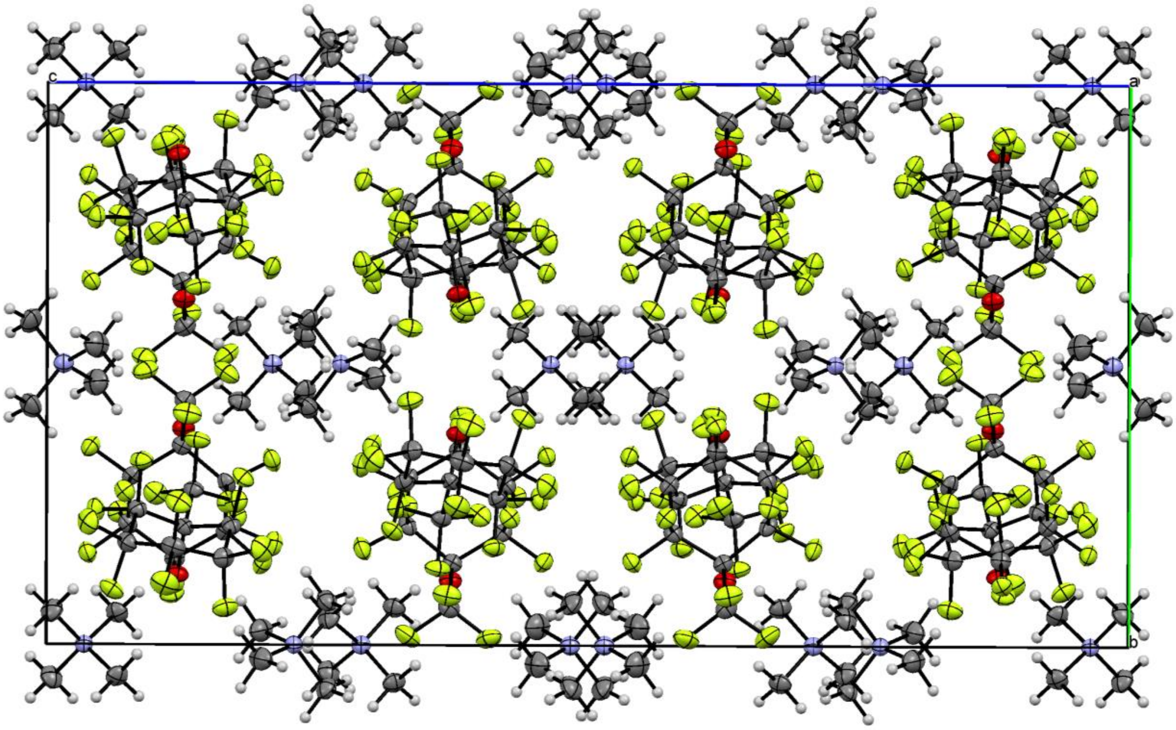


Figure 1-7: Unit cell of $[N(CH_3)_4]^+[C_7F_{13}O]^-$ with view along a.

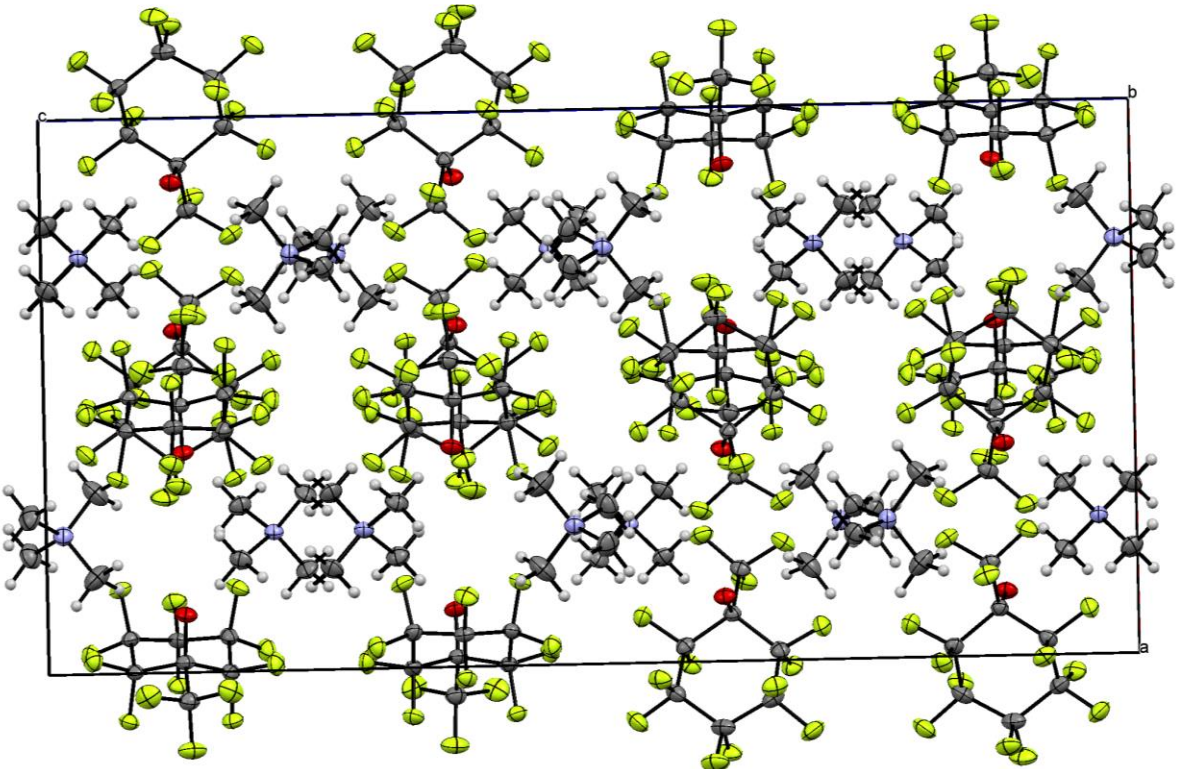


Figure 1-8: Unit cell of $[N(CH_3)_4]^+[C_7F_{13}O]^-$ with view along b.

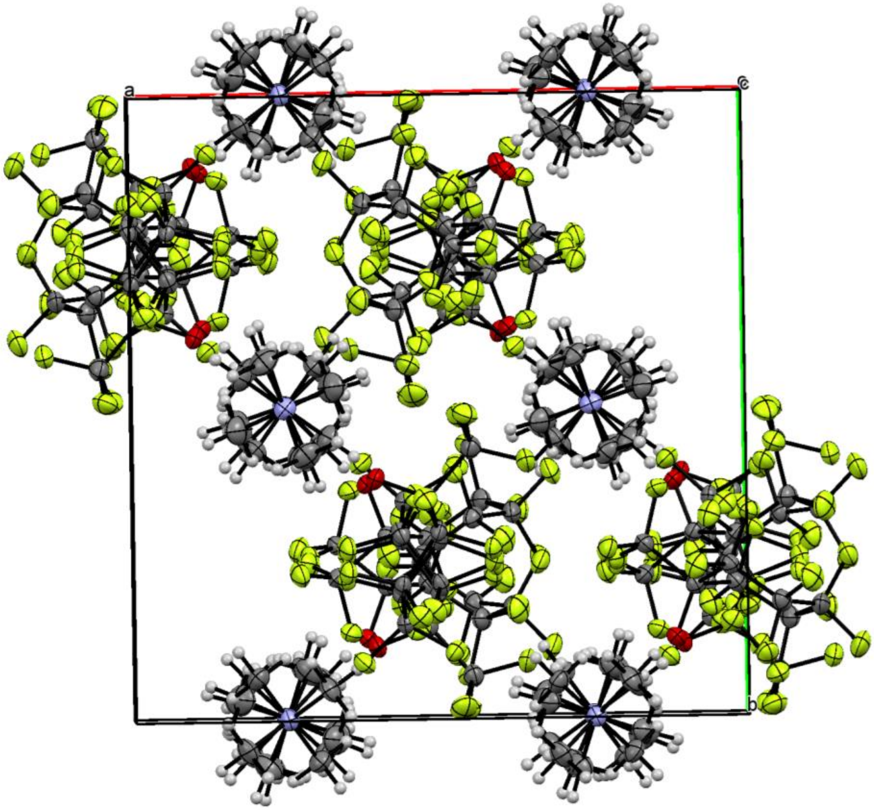


Figure 1-9: Unit cell of $[N(CH_3)_4]^+[C_7F_{13}O]^-$ with view along c.

1.5 Thermodynamics

The thermodynamic calculations were done with a combination to Born-Fajans-Haber-Cycles. An overall exergonic reaction resulted with $\Delta_\rho G° = -225.5$ kJ/mol. The individual values were determined in the following way and were summed up in Figure 1-10:

- Entropies in the gaseous phase were calculated using DFT on BP86[1, 2]/SV(P)[3]-level with the FREEH-tool.
- The fluoride ion was calculated by the Sackur-Tetrode-equation.[10]
- COSMO[11, 12] ($\varepsilon_r = 7{,}22$) was used on BP86/SV(P)-level to calculate free solvation energies.
- The Gibbs free energies in the gaseous phase were calculated with a combination of highly correlated calculations (G3-method[13]) on small molecules as well as an isodesmic reaction on BP86/SV(P)-level.

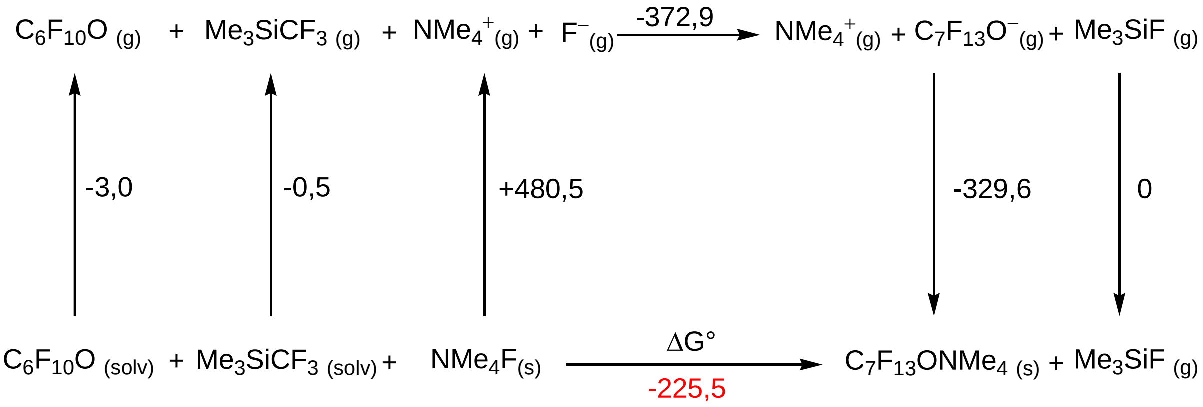


Figure 1-10: Born-Fajans-Haber-Cycle (BFHC) for the assessment of the total reaction: ΔG° in kJ/mol.

1.6 Hypothetic reaction mechanism

For a better understanding of this reaction, the reaction mechanism was tried to clarify. Thus, the reaction is only taking place, if [TMA]F was used in stoichiometric amounts. After 4 h $[N(CH_3)_4]^+[C_6F_{11}O]^-$ was detected as intermediate product next to $[N(CH_3)_4]^+[C_7F_{13}O]^-$. The first reaction step is the reaction of $C_6F_{10}O$ with [TMA]F to $[N(CH_3)_4]^+[C_6F_{11}O]^-$ as shown in the first step of Figure 1-11. The second step of the reaction could either occur by fluoride elimination and a trigonal-bypyramidal intermediate or as a cooperative mechanism.

To investigate this mechanism, calculations using DFT on BP86[1, 2]/SV(P)[3]-level with Turbomole[4, 5] were done. The results of the mechanism by fluoride elimination and a trigonal-bypyramidal intermediate are shown in Figure 1-11. This mechanism seems to be unlikely, due to the prohibitively endergonic step with +177.5 kJ/mol.

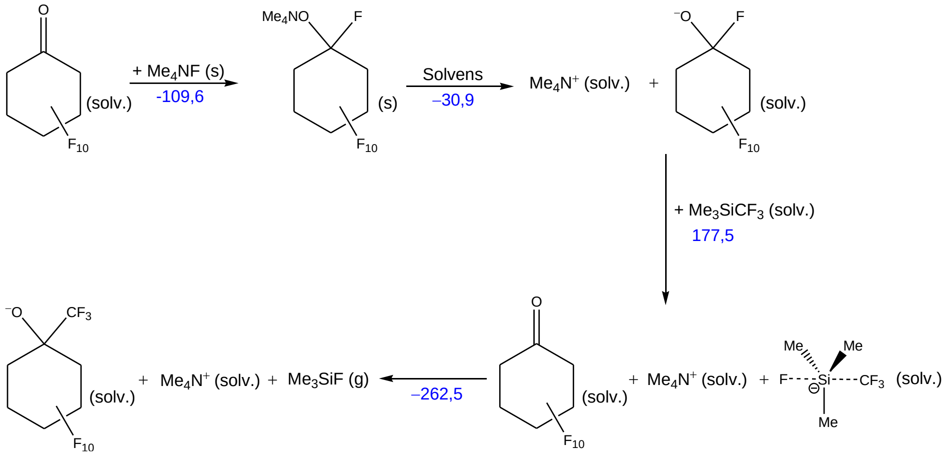


Figure 1-11: Calculated ΔG° values in $^{kJ}/_{mol}$ for the possible mechanism with fluoride elimination and a trigonal-bypyramidal intermediate.

The second possibility would be a cooperative step, where the silicon atom of Me_3SiCF_3 is coordinating to the negatively charged oxygen-atom and exchange a CF_3-group. This would couple the endergonic to the exergonic step and result in an exergonic step. The consulted step could look like it is drawn in Figure 1-12. This unusual mechanism would be driven by the enormous stability of the alkoxid $[N(CH_3)_4]^+[C_7F_{13}O]^-$. This is the more likely mechanism, due to the coupling of the endergonic to the exergonic step.

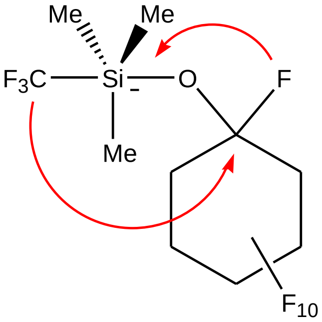


Figure 1-12: Me_3SiCF_3 coordination to the oxygen atom of the alkoxide-intermediate.

With the stoichiometric demand of the reaction in [TMA]F and complete conversion to $[N(CH_3)_4]^+[C_6F_{11}O]^-$ necessary for a complete reaction with $F_3C\text{-}SiMe_3$, this cooperative mechanism appears more likely.

2. $C_7F_{13}OH$

2.1 Synthesis

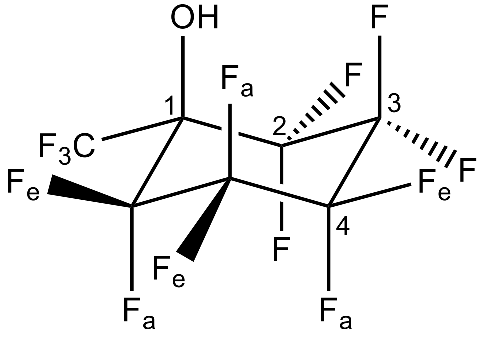
The synthesis was done in glass Schlenk-vessels and YOUNG®-NMR-tubes.

$[NMe_4]^+[C_7F_{13}O]^-$ (1.402 g, 3.328 mmol) was dissolved in concentrated H_2SO_4 (98 %; ca. 3 mL) at 25 °C. After stirring the solution for a short time, the NMR-spectra were measured at 25 °C. The pure isolated product $C_7F_{13}OH$ could be obtained in 60% yield (0.695 g, 1.997 mmol) through condensation as a colourless liquid.

2.2 Analysis with NMR-spectroscopy

The NMR data of $C_7F_{13}OH$ were obtained in CD_2Cl_2 at 298 K. In Table 2-1 the assignments of the NMR signals are shown. ^{19}F-shifts are given with respect to $CFCl_3$, ^1H and ^{13}C shifts with respect to TMS. In the following figures, the NMR spectra are shown. Individual coupling constants cannot be directly measured from line distances in the spectrum, because the spin system is an $AA'BB'CC'DD'EFG_3X$ and therefore of higher order. The great doublet splitting of the ^{19}F signals of the CF_2-groups for example results from a sum of more than one coupling constant, which is dominated by the $^2J_{F\text{-}F}$ coupling.

Table 2-1: NMR-shifts of $C_7F_{13}OH$ in CD_2Cl_2 at 298 K. Assignments are given with respect to the numbering scheme in the figure on the right.

	shift [ppm]	**multiplicity**	**assignment**	**Lewis structure of $C_7F_{13}OH$. Numbering Scheme.**
$\delta^{19}F$	-70.8	m	CF_3	
	-119.1	m	2a	
	-120.7	m	3a	
	-124.0	m	4a	
	-132.2	m	2e	
	-139.5	m	3e	
	-142.1	m	4e	
δ^1H	4.0	br ($\Delta\nu_{½}$= 9 Hz)	OH	
$\delta^{13}C$	74.4		1	
	110.7		2	
	107.9		3	
	107.2		4	
	120.8		CF_3	

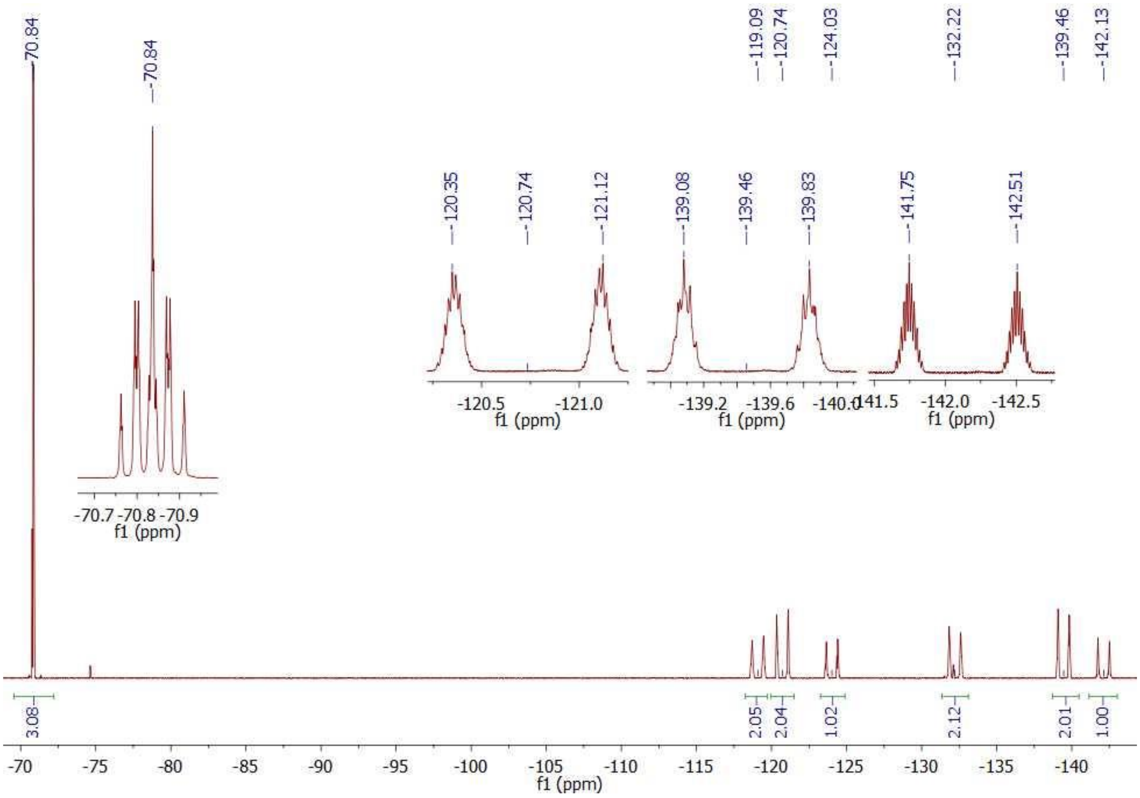


Figure 2-1: ${}^{19}F$-NMR spectrum (376.54 MHz) of $C_7F_{13}OH$ in CD_2Cl_2 at 298 K with detailed spectra of selected resonances.

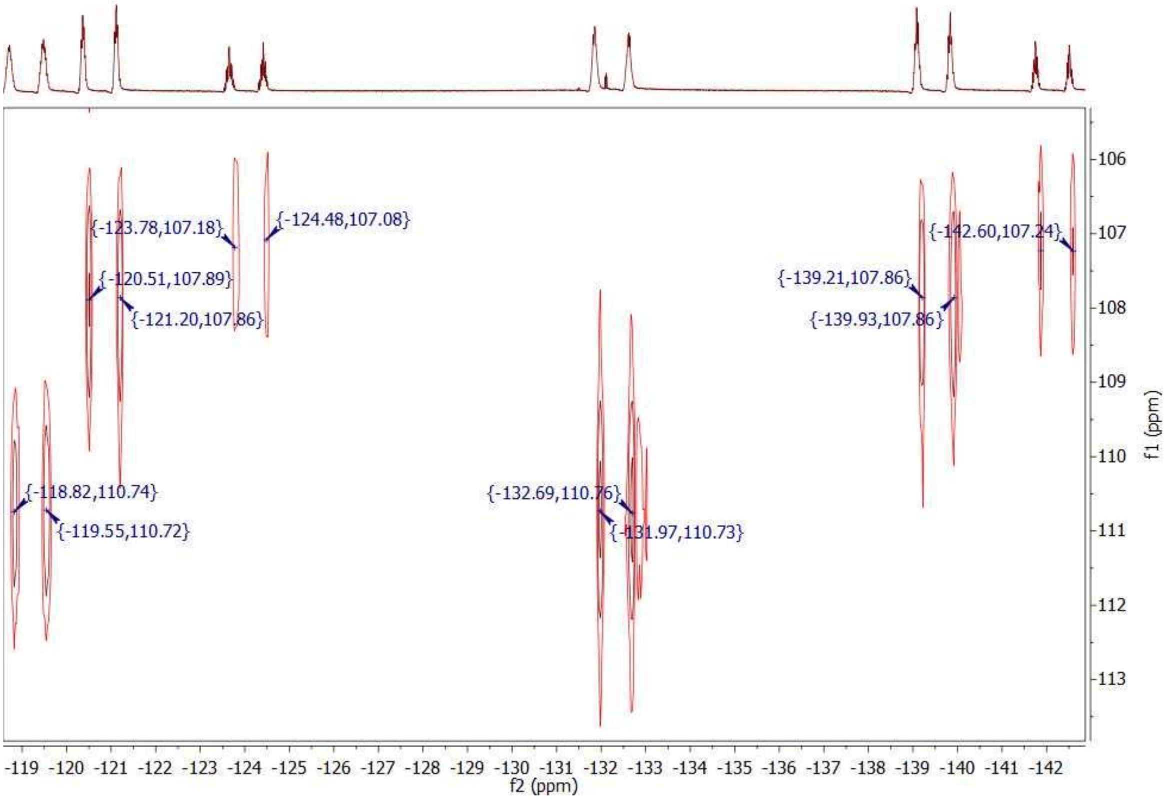


Figure 2-2: Selected area from the ${}^{19}F$,${}^{13}C$ HSQC NMR spectrum (376.54 MHz, optimized for ${}^{1}J_{F\text{-}C}$ couplings) of $C_7F_{13}OH$ in CD_2Cl_2 at 298 K. (${}^{19}F$ spectra plotted horizontal and ${}^{13}C$ spectra vertical).

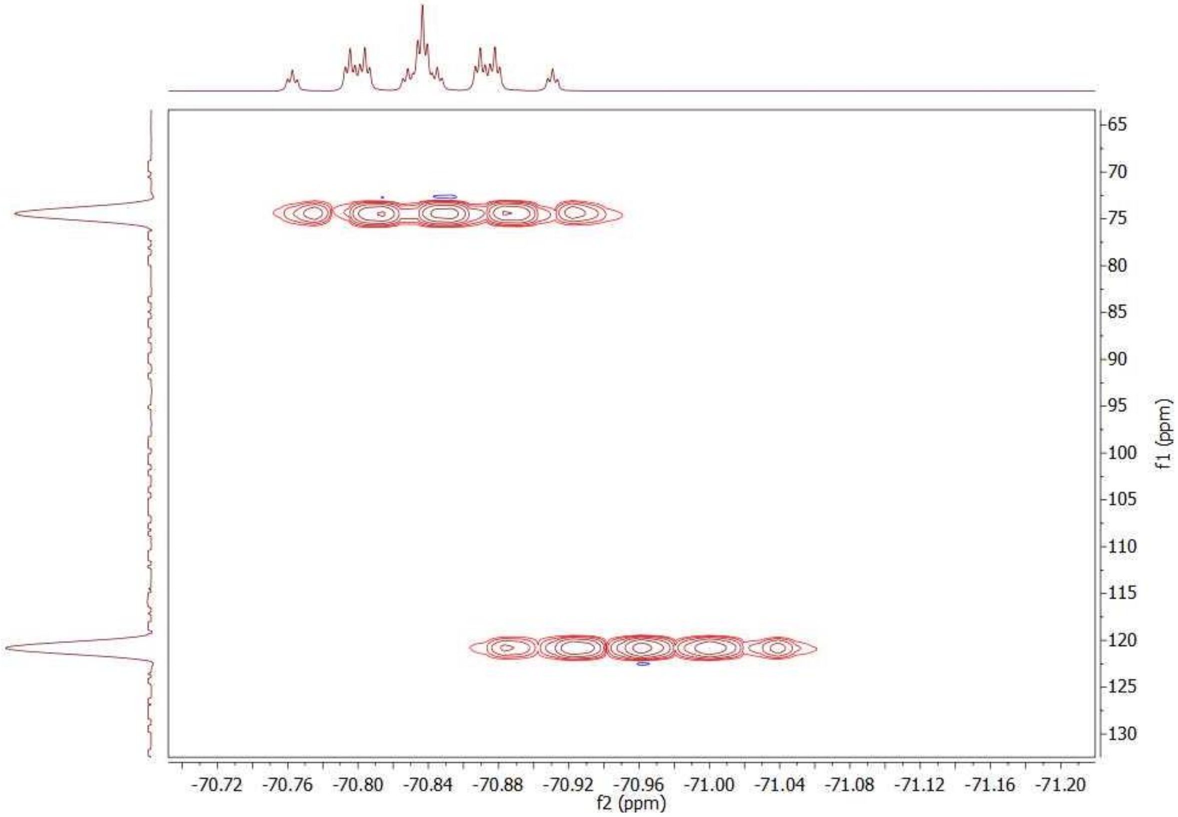


Figure 2-3: Selected area from the $^{19}F,^{13}C$ HSQC NMR spectrum (376.54 MHz, optimized for coupling constants of 40 Hz) of $C_7F_{13}OH$ in CD_2Cl_2 at 298 K. The crosspeak to the ^{13}C signal at 120.8 ppm results from a ^1J correlation (^{19}F spectra plotted horizontal and ^{13}C spectra vertical).

2.3 Single crystal X-ray diffraction analysis

A small amount 1-trifluoromethyl perfluorocyclohexane-1-ol was condensed into a self-made glass capillary and overlaid with pentane. From this mixture, a single crystal was grown manually by generating a crystal seed and cooling the sample to 200 K with 20 K/h and subsequently with 50 K/h to 100 K. A suitable crystal measured on an Agilent SuperNova, Single Source at offset, Eos diffractometer using Mo-Kα radiation (λ = 0.71073 Å) at 100.0(1) K. Using Olex2[14], the structure was solved with the ShelXT[15] structure solution program using Direct Methods and refined with the ShelXL[15] refinement package using least-square minimisation. More details are listed in Table 2-2 and Table 2-3. CCDC 1848204 contains the supplementary crystallographic data for this paper. These data can be obtained from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/conts/retrieving.htm.

Table 2-2: Summary of crystallographic data for 1-trifluoromethyl perfluorocyclohexane-1-ol ***1*** *x $^2/_3$ H_2O.*

	$(\mathbf{1})_3\cdot(H_2O)_2$
chemical formula	$C_{21}H_7F_{39}O_5$
M_r	1080.21
wavelength (Å)	Mo Kα (0.71073)
crystal system	monoclinic
space group	$P2_1/c$ (No.14)?
a (Å)	7.0390(4)

b (Å)	22.2491(13)
c (Å)	21.3552(12)
α (°)	90
β (°)	93.561(5)
γ (°)	90
V (Å^3)	432.066(9)
Z	4
Z'	1
T (K)	100.0(1)
ρ_{calc} (mg/mm^3)	2.150
μ (mm^{-1})	0.290
$2\Theta_{max}$ [°]	3.7 to 52.0
Index range h	$-8 \leq h \leq 8$
Index range k	$-27 \leq k \leq 27$
Index range l	$-26 \leq l \leq 26$
Refl. collect.	75798
Indep. refl.	6588
R_{int}	0.0690
Data/restraints/parameters	6588/0/614
R_1, $I>2\sigma(I)$ / all data[a]	0.0408/0.0204
wR_2, $I>2\sigma(I)$ / all data[b]	0.0825/0.0919
GoF	1.052
$\rho_{max/min}$ [e Å^{-3}]	0.34/-0.25

Table 2-3: Summary of hydrogen bonds for 1-trifluoromethyl perfluorocyclohexane-1-ol ***1*** *x $^{2}/_{3}$ H_2O.*

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1	H1	O4	0.76(3)	1.98(3)	2.705(3)	160(3)
O3	H3	O4	0.73(3)	1.99(4)	2.711(3)	168(4)
O2	H2	O5	0.79(3)	1.92(3)	2.643(3)	153(3)
O4	H4A	O5[c]	0.72(3)	2.27(3)	2.920(3)	150(3)
O4	H4B	F16[c]	0.82(4)	2.54(4)	3.279(3)	150(3)
O4	H4B	O2[c]	0.82(4)	2.18(4)	2.843(2)	137(3)
O5	H5A	F35	0.82(3)	2.62(3)	3.314(3)	144(3)
O5	H5A	O3	0.82(3)	2.22(3)	2.961(3)	150(3)
O5	H5B	O1	0.75(4)	2.28(4)	2.938(3)	147(3)

---

[a] R_1 is defined as $\Sigma||F_o|-|F_c||/\Sigma |F_o|$ for $I > 2\sigma(I)$.

[b] wR_2 is defined as $[\Sigma w\{F_o^2 - F_c^2\}^2/\Sigma w(F_o^2)^2]^{1/2}$ for $I > 2\sigma(I)$.

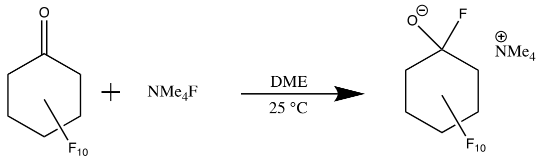
[c] 1+X, +Y, +Z

3. $[N(CH_3)_4][C_6F_{11}O]$

3.1 Synthesis

The synthesis {1} was done once in a glass Schlenk flask and once in a T-reactor out of PFA with a diameter of ½” or ¼”, which were closed with a KEL-F valve. Prior synthesis the vessels were dried using anhydrous HF. The PFA vessels were used to secure that glass is not directly eliminating HF.

NMe_4F (60.6 mg, 0.6 mmol, 1.0 eq) was weighed and handled in glove box. Anhydrous dimethoxyethane (DME) (1.2 mL) was transferred using a syringe at a glass-vacuum line. As third decafluorocyclohexanon ($C_6F_{10}O$) (0.65 mmol, 1.0 eq) was condensed onto the mixture at –40 °C. The reaction was running 15 h with occasional mixing of the liquid at 25 °C. Afterwards DME was removed using dynamic vacuum at room temperature. A colourless powder was obtained, which analyses according to Raman spectroscopy and a single crystal structure determination as $[NMe_4]^+[C_6F_{11}O]^-$. It was not analysed further.



{1}

3 **5**

3.2 Analysis with vibrational spectroscopy

As vibrational analysis IR and Raman spectroscopy was used. The experimental data are shown in Figure 3-1 and the assignment was done in Table 3-1. The calculation was done using DFT on def2-TZVPP[16]-level with Turbomole[4, 5]. In addition, the module AORORCE[6, 7] was used to calculate the frequencies on analytical level. The calculations were done for the OH in axial and in equatorial position.

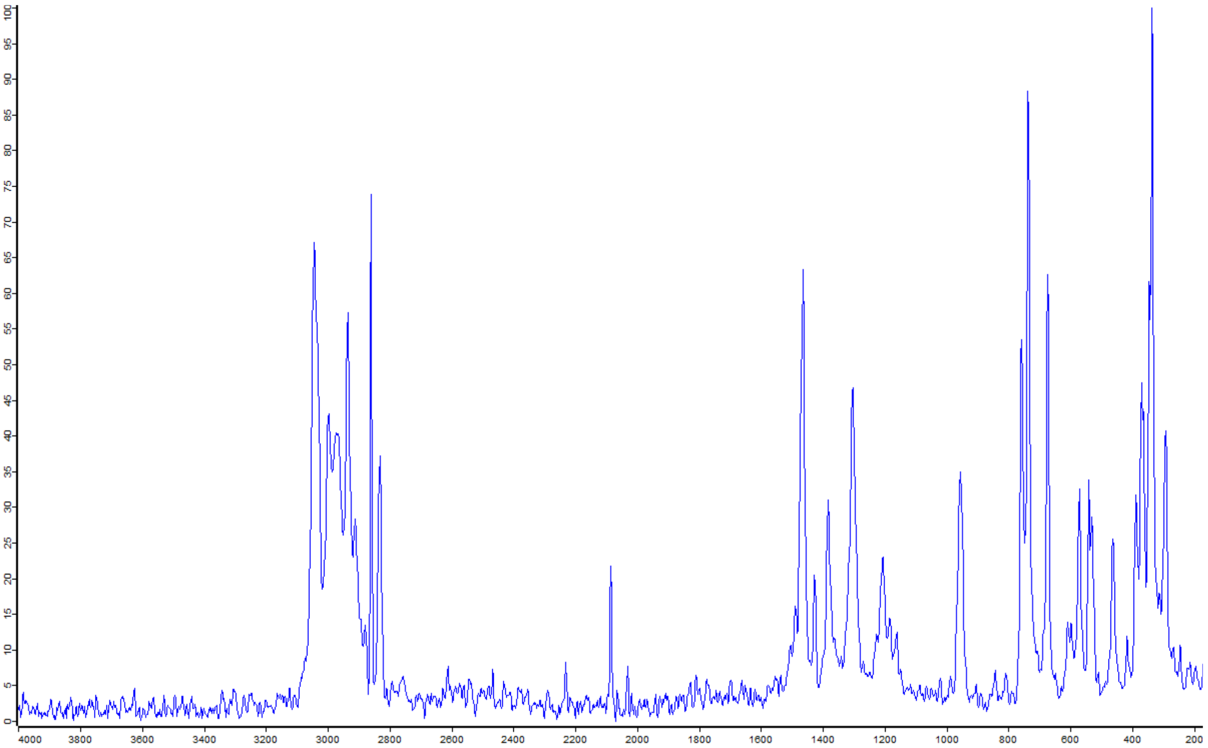


Figure 3-1: Raman spectra of $[N(CH_3)_4]^+[C_6F_{11}O]^-$. The Raman was measured in vacuum at low temperature.

Table 3-1: experimental IR and calculated vibrational data of $[NMe_4]^+[C_6F_{11}O]^-$.

$[N(CH_3)_4]^+$		**$[C_6F_{11}O]^-$**		
assignment	**Raman** (exp) [cm^{-1}]	**Raman** (exp) [cm^{-1}]	**vibration** (cal.) [cm^{-1}]	**assignment**
$[N(CH_3)_4]^+$	3073 (vw)	1424 (m)	1425	υ_{s}(CO)
$[N(CH_3)_4]^+$	3043 (s)	1302 (m)	1304	υ_{s}(CC)
$[N(CH_3)_4]^+$	3032 (m, sh)	-	1292	υ_{as}(CC)
$[N(CH_3)_4]^+$	2997 (m)	-	1290	υ_{as}(CC)
$[N(CH_3)_4]^+$	2972 (m)	-	1276	υ_{as}(CC)
$[N(CH_3)_4]^+$	2966 (m)	1224 (w)	1230	υ_{as}(CC)
$[N(CH_3)_4]^+$	2935 (s)	1204 (m)	1196	υ_{s}(CC)
$[N(CH_3)_4]^+$	2911 (m)	1181 (w)	1179	υ(CF)
$[N(CH_3)_4]^+$	2893 (vw)	1159 (w)	1159	υ(CF)
$[N(CH_3)_4]^+$	2878 (vw)	1147 (vw)	1137	υ(CF), υ_{as}(CC)
$[N(CH_3)_4]^+$	2859 (vs)		1122	υ(CF), υ_{as}(CC)
$[N(CH_3)_4]^+$	2830 (m)	-	1095	υ(CF), υ_{as}(CC)
$[N(CH_3)_4]^+$	2611 (vw)	-	1082	υ_{s}(CF)
$[N(CH_3)_4]^+$	2230 (vw)	1018 (vw)	1015	υ_{as}(CF), υ_{as}(CC)
$[N(CH_3)_4]^+$	2093 (vw)	986 (vw)	991	δ (CCF)
$[N(CH_3)_4]^+$	2084 (w)	954 (m)	967	υ(CF)
$[N(CH_3)_4]^+$	2029 (vw)	-	923	υ(CF)
$[N(CH_3)_4]^+$	1486 (w)	-	861	δ (CCF)
$[N(CH_3)_4]^+$	1462 (s)	682 (w, sh)	682	δ (FCF), δ (FCO)

$[N(CH_3)_4]^+$	1381 (m)	670 (s)	672	δ_s(FCF)
$[N(CH_3)_4]^+$	756 (s)	-	626	δ_{as}(FCF)
$[N(CH_3)_4]^+$	734 (vs)	-	614	δ_{as}(FCF) , δ(FCO)
$[N(CH_3)_4]^+$	538 (m)	606 (w)	601	δ_{as}(FCF) , δ(FCO)
$[N(CH_3)_4]^+$	386 (m)	595 (w)	592	δ_{as}(FCF)
		568 (m)	550	δ_{as}(FCF)
		460 (m)	472	δ_{as}(FCF)
		448 (vw, sh)	458	δ_{as}(FCF)
		414 (w)	416	δ_{as}(FCF)
		368 (m)	369	Rocking CF_2
		361 (m)	359	Rocking CF_2
		342 (s, sh)	345	Rocking CF_2
		333 (vs)	334	Rocking CF_2
		324 (w, sh)	328	Framework vib
		309 (w)	307	Wagging CF_2
		-	306	Wagging CF_2
		-	296	Wagging CF_2
		289 (m)	287	Wagging CF_2
		242 (vw)	243	Wagging CF_2

3.3 Single crystal X-ray diffractometric analysis

The crystals of $NMe_4^+[C_6F_{11}O]^-$ were obtained by recrystallization in CH_2Cl_2. In the following the crystal data and structure refinement parameters are shown in Table 3-2, the asymmetric unit in Figure 3-2 as well as the unit cell along direction a (Figure 3-4), b (Figure 3-5) and c (Figure 3-6).

Table 3-2: Crystal data and structure refinement parameters for $[N(CH_3)_4]^+[C_6F_{11}O]^-$

Compound	**$NMe_4^+C_6F_{11}O^-$**
CCDC	1839048
Empirical formula	$C_{10}H_{12}F_{11}NO$
Formula weight	371.21
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.4929(2)
b/Å	10.3291(2)
c/Å	18.0550(4)
α/°	90
β/°	94.4750(10)
γ/°	90
Volume/Å^3	1393.11(6)
Z	4
ρ_{calc}g/cm^3	1.770
μ/mm^{-1}	0.213
F(000)	744.0

Crystal size/mm^3	0.11 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.546 to 60.044
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -25 ≤ l ≤ 25
Reflections collected	29035
Independent reflections	4062 [R_{int} = 0.0285, R_{sigma} = 0.0176]
Data/restraints/parameters	4062/0/244
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0340, wR_2 = 0.0857
Final R indexes [all data]	R_1 = 0.0418, wR_2 = 0.0904
Largest diff. peak/hole / e Å^{-3}	0.52/-0.25

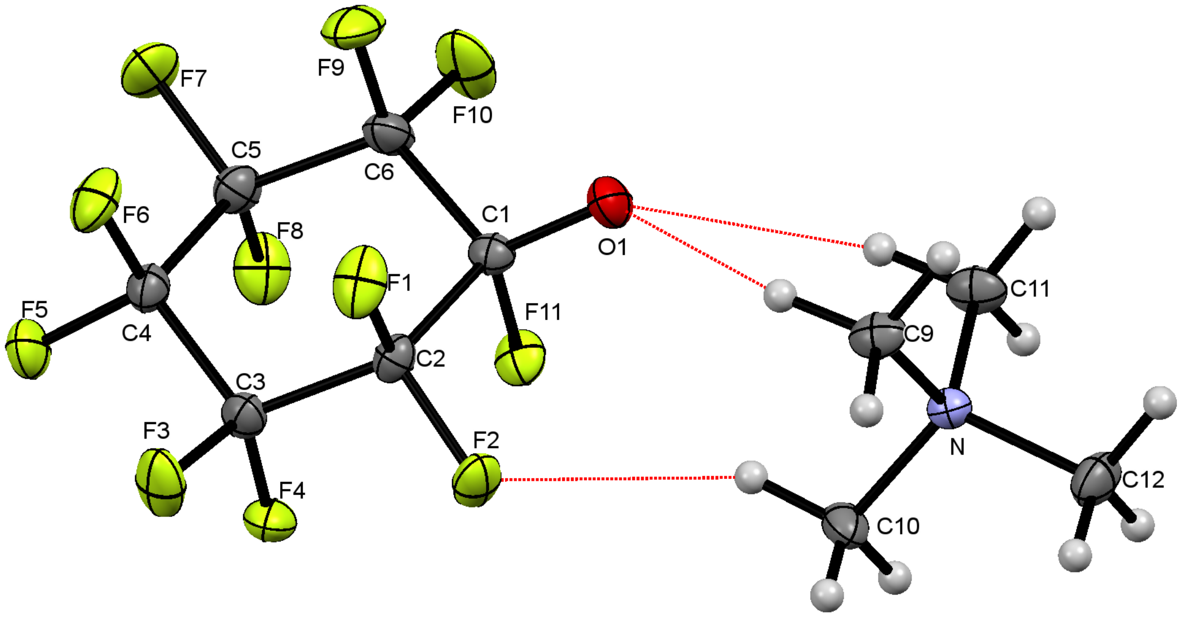


Figure 3-2: asymmetric unit of $[N(CH_3)_4]^+[C_6F_{11}O]^-$.

The C-C bonds are in a range of 1.532(2) (C3-C4) to 1.563(2) Å (C2-C1), which is rather long for a C-C singe bond. The previously published perfluoro-alkylalcohol $(F_5C_6)(F_{10}C_5)COH$ is with an average aliphatic C-C-bond length of 1.556(5) Å in the same range.[8] Also Heptafluorocyclobutanol, another perfluoro-alkylalcohol is showing C-C-bond lengths in in the same order.[9]

The C-O bond is 1.257(1) Å and is significantly shorter than a typical C-O single bond. Instead it is more in the magnitude of a C=O double bond. It is still shorter than the C-O bond in $[NMe_4]^+[C_7F_{13}O]^-$ (1.328(3) Å). It is conspicuous that the bond between C1 and F11 is with 1.489(1) Å very long compared to all other CF bonds of the molecule. They are ranging from 1.344(1) (C5-F8) till 1.357(1) Å (C6-F9), which is in a normal range for perfluoro-alkylalcohols and also similar to the previously described $[NMe_4]^+[C_7F_{13}O]^-$.[8, 9] This leads to an assumption that the molecule could be more likely be described as the ketone with an added F^-. Also in comparison to the only known crystal structure of an α-fluoroalcohol, heptafluorocyclobutanol, where the CF bond at C1 is 1.362(4) Å.[9]

To demonstrate the correct assignment of the atoms, we have done further refinements of the single crystal x-ray data set and show the residual electron densities for alternative assignments of O1 and F11 in the following Figure 3-3. It follows, that only the assignment in the middle below is in good agreement with the experiment and it has least remaining residual electron densities.

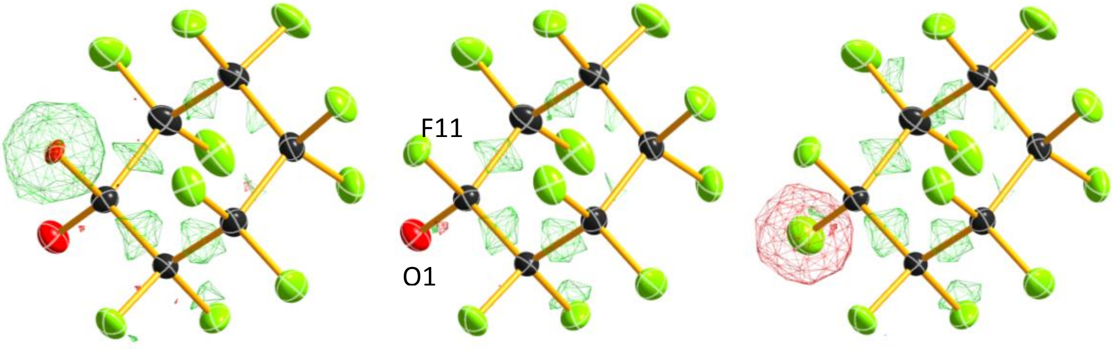


Figure 3-3: showing of the remaining electron density if F11 would be an Oxygen Atom (left), If F11 is fluorine and O1 is Oxygen (middle) and if O1 would be an fluorine Atom (right). The remaining electron density is shown as doted sphere with Fo-Fc of 0.20 e/Å^3 and a map radius of 3.20 Å.

There are several further evidences, that O1 is in equatorial and F11 in axial position:

- Moreover, the bond lengths are an evidence for this orientation. The C1-O1 bond is with 1.257(1) Å too short for an CF bond and the C1-F11 bond is with 1.489(1) Å to long for an C-O single bond.[17]
- The calculated difference between O1 in equatorial and axial position is +3.59 $^{kJ}/_{mol}$. The calculation was done using DFT with def2-TZVPP[16]-basis set with Turbomole[4, 5].

Thus, we are confident that our assignment is correct.

All C-C-C-angles are in between 109.9(9) (C6-C1-C2) and 117.1(9)° (C5-C6-C1). The F-C-F angle are ranging from 106.9(9) (F2-C2-F1) to 107.9(9)° (F6-C4-F5). The CCF-angel are in a range of 100.2(8) (F11-C1-C2) and 110.2(9)° (F4-C3-C2). The FCO angle is 114.0(9)°. All observed angles are similar to $[NMe_4]^+[C_7F_{13}O]^-$ and literature values.[8, 9]

The anions are connected via intermolecular hydrogen bonding from fluorine to the Carbons of the cations. Each cation is bonded to different anions and vice versa. The anion is present in a chair conformation with oxygen in equatorial position.

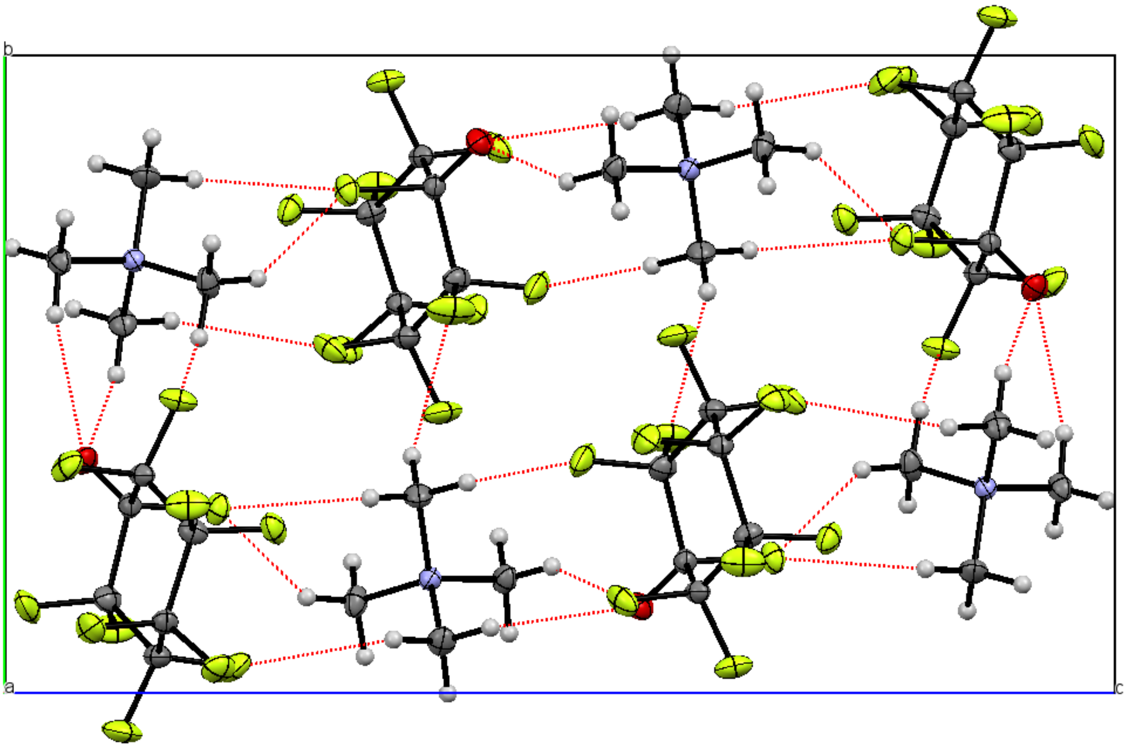


Figure 3-4: Unit cell of $[N(CH_3)_4]^+[C_6F_{11}O]^-$ with view along a.

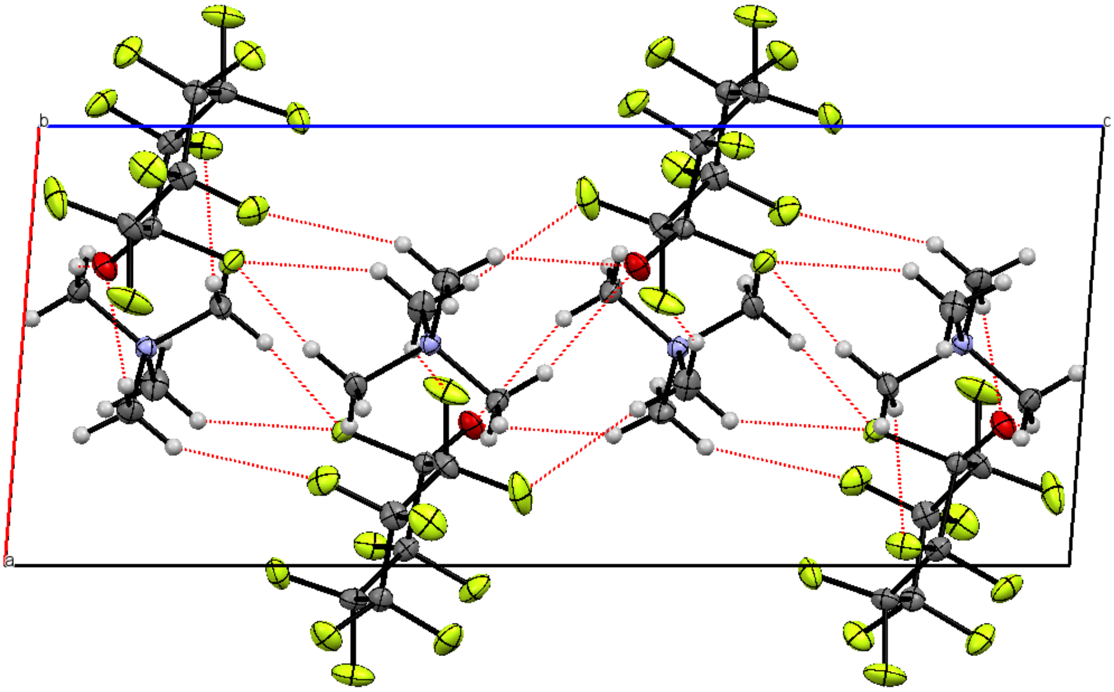


Figure 3-5: Unit cell of $[N(CH_3)_4]^+[C_6F_{11}O]^-$ with view along b.

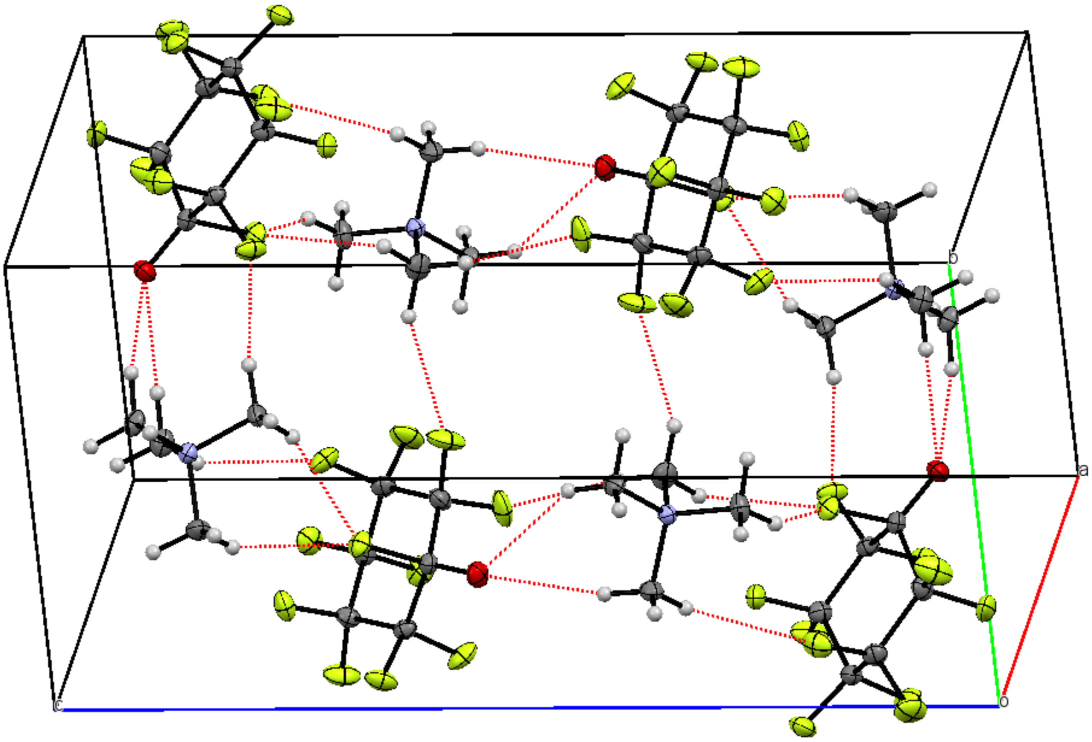


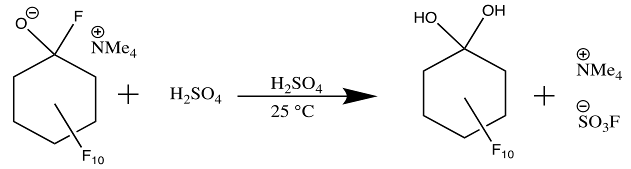
Figure 3-6: Unit cell of $[N(CH_3)_4]^+[C_6F_{11}O]^-$ as 3-dimensional view.

4. Decafluorocyclohexan-1,1-diol (6): $C_6F_{10}(OH)_2$

4.1 Synthesis

The synthesis {2} was done once in glass Schlenk-flask, YOUNG®-NMR-Tube and once in a T−reactor made from PFA with a diameter of $^1/_8$” or ¼”. It was closed with KEL-F valves. Prior to synthesis, the vessels were dried using anhydrous HF.

NMe_4F (5.19 g, 16.8 mmol, 1.00 eq) was weighed and handled in glove box. Anhydrous dimethoxyethane (DME) (50 mL) was transferred using a syringe at a glass-vacuum line. As third decafluorocyclohexanon ($C_6F_{10}O$) (5.06 g, 18.2 mmol, 1.08 eq) was condensed onto the mixture at −30 °C. The reaction was running 15 h with occasional mixing of the liquid at 25 °C. Afterwards DME was removed using dynamic vacuum at room temperature. $[NMe_4]^+[C_6F_{11}O]^-$ was obtained as colourless powder, which was dissolved in concentrated H_2SO_4 (ca. 4 mL) at 25 °C. After stirring the solution for a short time, the NMR-spectra were measured at 25 °C. The pure isolated product $C_6F_{10}(OH)_2$ could be obtained in 63 % (3.11 g, 10.5 mmol) yield through sublimation and recrystallization in dichloromethane (CH_2Cl_2). Colourless block shaped crystals were obtained for single crystal X-ray diffractometry.



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{2}

4.2 Analysis with vibrational spectroscopy

As vibrational analysis IR and Raman spectroscopy was used. The experimental data are shown in Figure 4-1 and the assignment was done in Table 4-1. The calculation was done using DFT on BP86[1, 2]/SV(P)[3]-level with Turbomole[4, 5]. In addition, the module AORORCE[6, 7] was used to calculate the frequencies on analytical level.

Table 4-1: experimental IR and calculated vibrational data of $C_6F_{10}(OH)_2$.

IR (exp.) [cm^{-1}]	**Raman** (exp) [cm^{-1}]	**$C_6F_{10}(OH)_2$** (cal.)	**assignment**
3586 (w)	-	3790	υ_s(OH)
	-	3786	υ_{as} (OH)
3474 (w)	-	-	H_2O
1396 (vw)	1394 (vw)	1399	δ_s (COH)
-	-	1368	δ_{as} (COH)
1313 (m)	1315 (m)	1311	υ_s (CC)
-	-	1295	υ_{as} (CC)
-	-	1293	υ_{as} (CC)
1249 (m)	1240 (w)	1239	υ_{as} (CC)
1230 (m, sh)	-	1231	υ_{as} (CC)
-	-	1226	υ_{as} (CC)

1213 (s)	-	1213	υ_{s} (CC)
1176 (s)	1180 (w)	1175	υ_{s} (CC)
-	1164 (w)	1166	υ_{as} (CC)
-	1149 (w)	1165	υ_{as} (CC)
1157 (m)	-	1160	υ_{as} (CC)
-	-	1131	υ_{as} (CC)
1119 (m)	-	1120	υ_{as} (CC)
-	1051 (vw)	1045	υ_{as} (CC)
1036 (m)	1043 (vw)	1034	υ_{as} (CC)
960 (s, sh)	-	973	υ_{as} (CF)
937 (vs)	-	936	δ_{s} (FCF)
844 (vw)	-	838	δ_{s} (FCF)
690 (vw)	691 (vs)	690	δ (FCF)
678 (w)	-	676	δ (FCF)
-	-	637	δ (FCF)
632 (s)	-	632	δ (FCF)
600 (vw)	600 (w)	602	δ (FCF)
-	-	598	δ (FCF)
567 (vw)	568 (m)	560	δ (FCF)
-	-	482	δ (COH)
471 (s)	-	473	δ (FCC)
-	-	432	δ (COH)
418 (w)	-	404	δ (COH)
-	374 (s)	373	Framework vib
-	338 (s)	340	twisting OH
-	314 (w, sh)	312	Framework vib
-	289 (m)	288	Framework vib
-	276 (vw, sh)	280	twisting OH
-	249 (w)	249	Framework vib
-	196 (w)	193	Framework vib
-	168 (w)	173	Framework vib

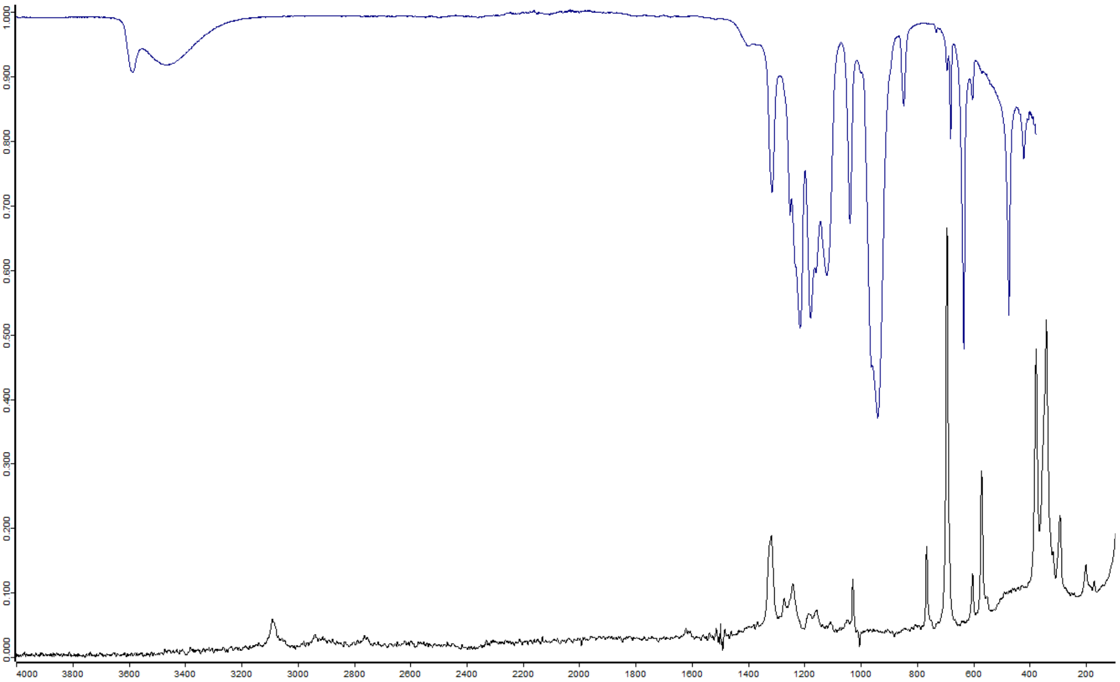
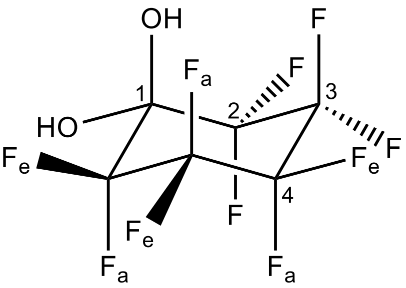


Figure 4-1: Raman (black, bottom) and IR spectrum (blue, top). The OH vibrations in the IR spectrum are a broad signal, probably due to partially occurring H-bonding (see crystal structure).

4.3 Analysis with NMR-spectroscopy

The NMR data of $C_6F_{10}(OH)_2$ were obtained in CD_2Cl_2 at 298 K. In Table 4-2 assignments of the NMR signals are shown. ^{19}F-shifts are given with respect to $CFCl_3$, ^1H and ^{13}C shifts with respect to TMS. In the following figures, the NMR spectra are shown. The ^{19}F-resonances can't be assigned to single fluorine atoms, because there is only a very broad coalescence signal with centre at about –132 ppm, a width of 1600 Hz and without fine structure (see Figure 4-2).

Table 4-2: NMR-shifts of $C_6F_{10}(OH)_2$ in CD_2Cl_2 at 298 K. Assignment according to the numbering scheme shown in the figure on the right.

	shift [ppm]	**multiplicity**	**assignment**	**Lewis structure of $C_6F_{10}(OH)_2$. Numbering Scheme.**
$\delta^{19}F$	-132	br ($\Delta\nu_{½}$= 1600 Hz)	-	
$\delta^{1}H$	3.94	s	OH	
$\delta^{13}C$	90.8		1	
	110.2		2	
	108.1		3	
	107.8		4	

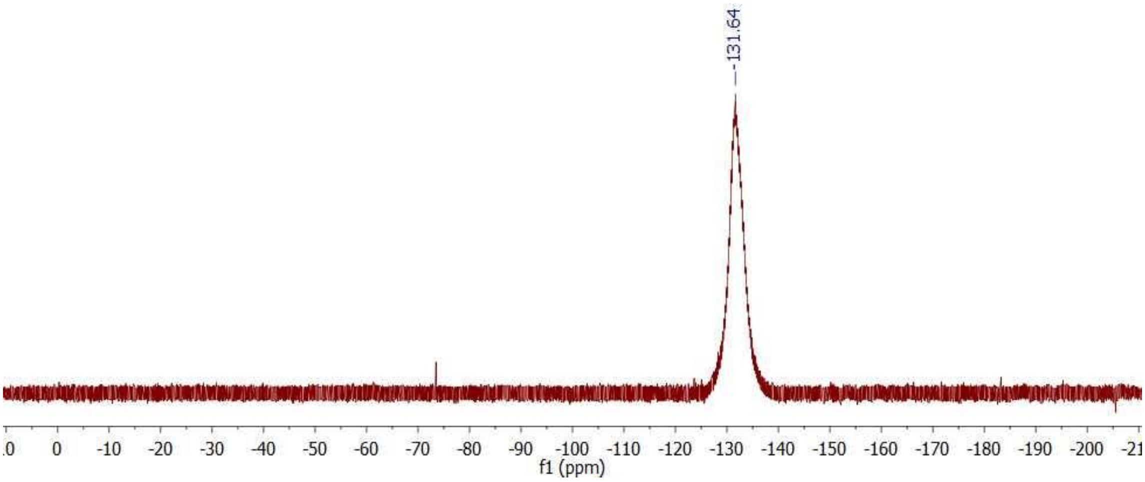


Figure 4-2: ^{19}F-NMR spectrum (282.45 MHz) of $C_6F_{10}(OH)_2$ in CD_2Cl_2 at 298 K.

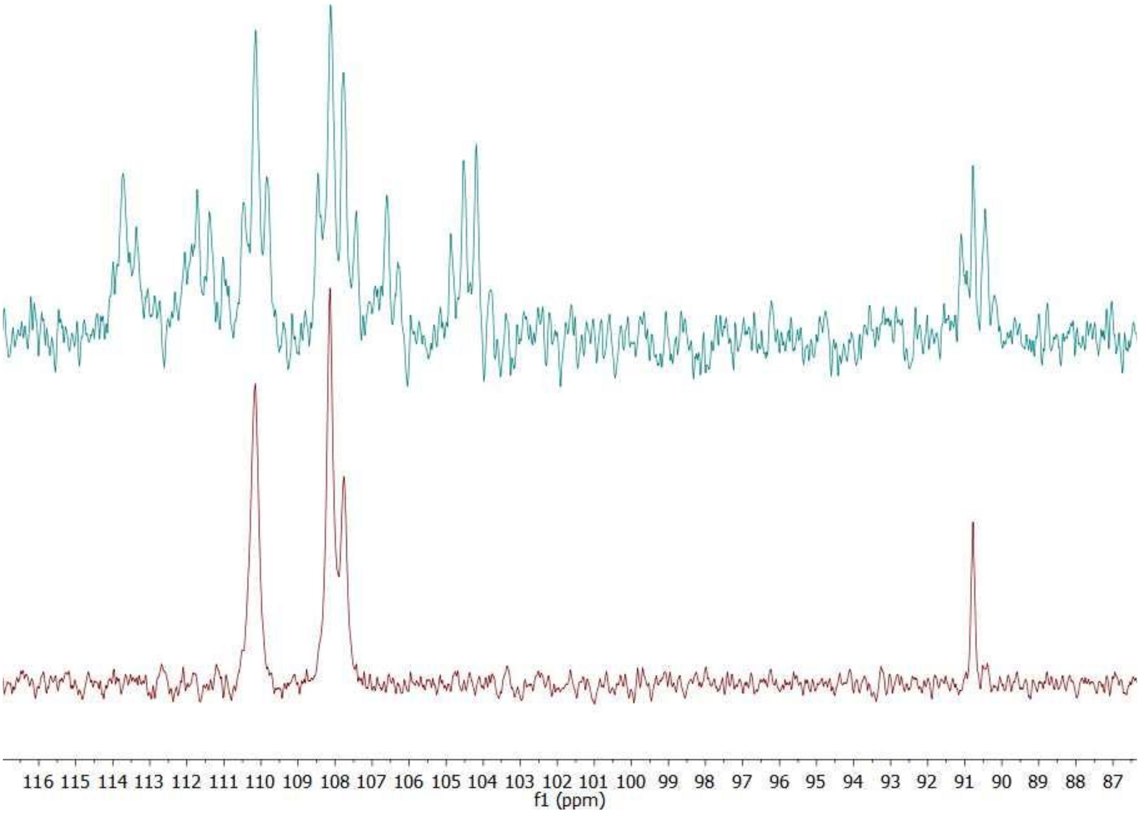
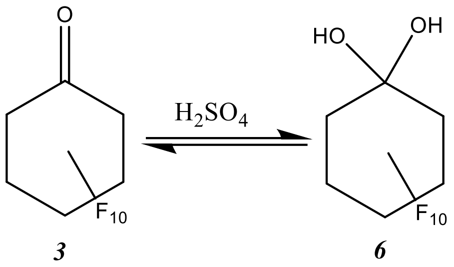


Figure 4-3: Selected area from the ^{13}C NMR spectra (75.48 MHz) of $C_6F_{10}(OH)_2$ in CD_2Cl_2 at 298 K ^{19}F-decoupled (bottom, 1) and ^{19}F-coupled (top, 2).

4.4 Decafluorocyclohexanon in sulphuric acid

To clarify the mechanism of reaction {2} (see chapter 4.5), sulphuric acid (96%) was mixed with **3** (equation {3}). The two liquids do not form a uniform solution. Several drops of **3** were dispersed in sulphuric acid. The ^{19}F signals of the starting material in Figure 4-4 result from these drops, whereas the broad ^{19}F resonance at about −131 ppm belongs to the product ***6***. The presence of ***6*** is unambiguously proven by the ^{13}C signal at 91 ppm in the ^{13}C NMR spectrum in Figure 4-5. Thus **3** is able to dehydrate concentrated sulphuric acid forming ***6***.



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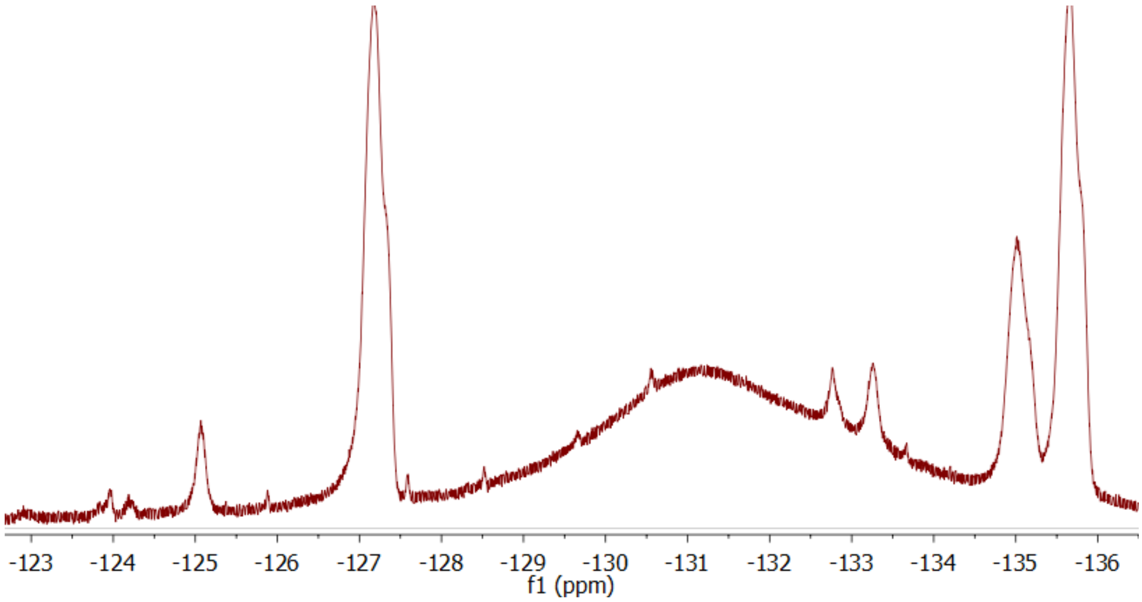


*Figure 4-4: ^{19}F NMR spectrum (188.29 MHz) of the inhomogeneous mixture of **3** in H_2SO_4 at 298 K. The three signals at −127, −135 and −135.7 belong to the starting material. The broad signal at about −131 ppm with a width of 780 Hz is the coalescence signal of the fluorine atoms of **6**.*

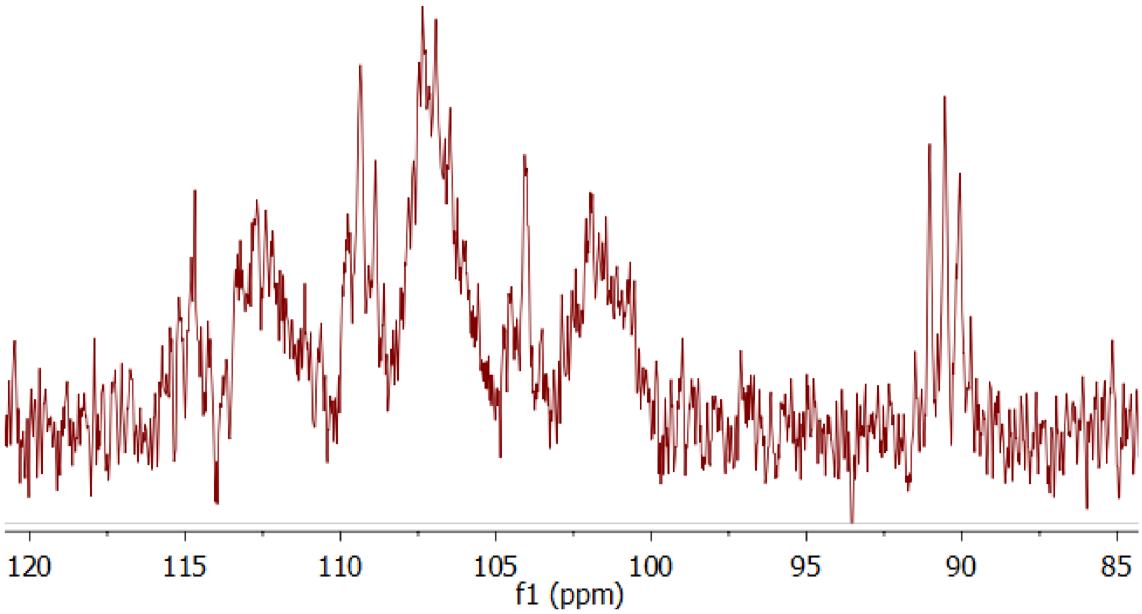


*Figure 4-5: Selected area from the ^{13}C NMR spectrum (50.33 MHz) of the inhomogeneous mixture of **3** in H_2SO_4 at 298 K. The signal at 91 ppm proves the formation of* **6***.*

4.5 mechanism

First the evidences to form a mechanism are summarized:

- ***3*** + H_2SO_4 → ***6***
- ***4*** + H_2SO_4 → ***1***
- ***5*** + H_2SO_4 → ***6***
- ***2*** → **3** + HF (H^0= 78.1 kJ mol^{-1}, G^0 = 31.8 kJ mol^{-1})
- ***2*** is decomposing with non-inert atmosphere
- the C1-F11 bond of ***5*** is very long and C1-O1 has double bond character.

From these evidences the mechanism, shown in Figure 4-6, was postulated. The single steps were calculated using PBEh-3c method implemented with ORCA 4.0.

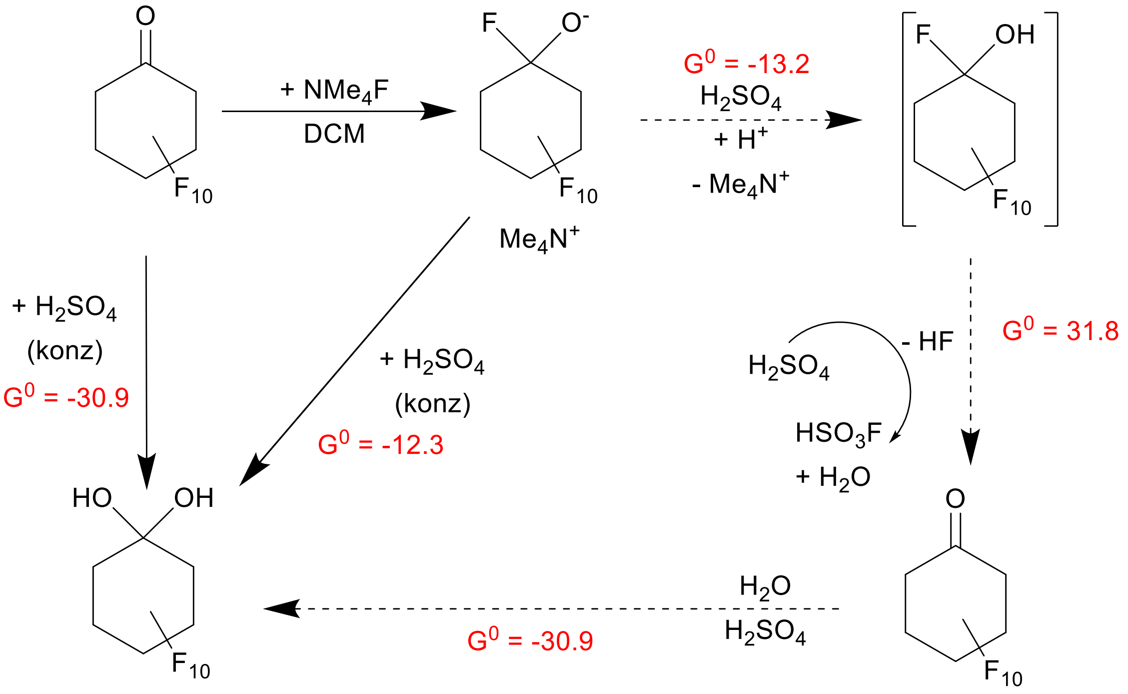


Figure 4-6: postulated mechanism for reaction {2} and calculated reaction enthalpies in kJ mol^{-1}.

4.6 Single crystal X-Ray diffraction

The crystals of $C_6F_{10}(OH)_2$ were obtained by recrystallization in CH_2Cl_2. In the following the crystal data and structure refinement parameters are shown in Table 4-3, the asymmetric unit in Figure 4-7 as well as the unit cell along direction a (Figure 4-8), b (Figure 4-9) and c (Figure 4-10).

Table 4-3: Crystal data and structure refinement parameters for $C_6F_{10}(OH)_2$

Compound	**$C_6F_{10}(OH)_2$**
CCDC	1839049
Empirical formula	$C_6H_2F_{10}O_2$
Formula weight	296.08
Temperature/K	100.02

Crystal system	orthorhombic
Space group	Pca2$_1$
a/Å	10.3768(4)
b/Å	20.2598(6)
c/Å	8.3401(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1753.35(11)
Z	8
ρ_{calc}g/cm^3	2.243
μ/mm^{-1}	0.297
F(000)	1152.0
Crystal size/mm^3	0.2 × 0.12 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.02 to 54.98
Index ranges	$-13 \leq h \leq 13$, $-26 \leq k \leq 26$, $-10 \leq l \leq 10$
Reflections collected	18866
Independent reflections	4001 [R_{int} = 0.0228, R_{sigma} = 0.0176]
Data/restraints/parameters	4001/7/333
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0258, wR_2 = 0.0669
Final R indexes [all data]	R_1 = 0.0283, wR_2 = 0.0685
Largest diff. peak/hole / e Å^{-3}	0.45/-0.24
Flack parameter	0.0(3)

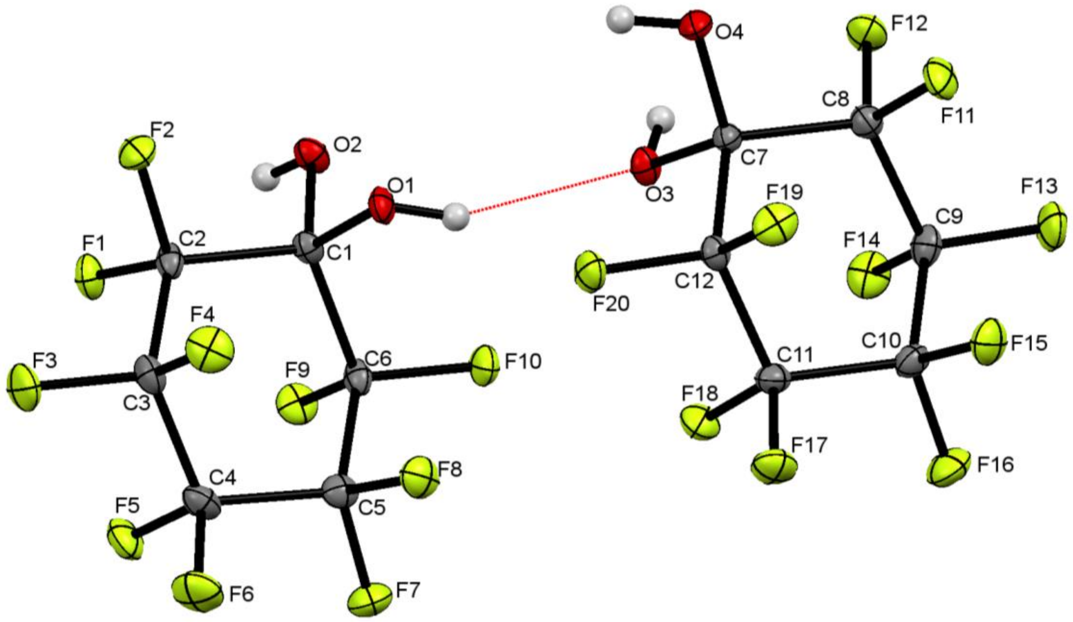


Figure 4-7: Asymmetric unit of $C_6F_{10}(OH)_2$ with two formula units.

The C-C bonds are in a range of 1.539(4) (C6-C5) and 1.552(4) Å (C1-C6), which is rather long for a C-C singe bond. The previously mentioned alkoxides are in the same magnitude. Also hexafluorocyclobutan-1,1-diol, another perfluoro-alkyldiol is showing C-C-bond lengths in in the same order.[9]

The C-O bond is between 1.380(3) Å and 1.406(3) Å and in a normal range for an C-O single bond[17] and is similar to hexafluorocyclobutan-1,1-diol.[9] The C-F bonds are ranging from 1.334(3) Å (C10-F16) till 1.354(3) Å (C6-F10), which is similar to the previously described $[NMe_4]^+[C_7F_{13}O]^-$ and $[NMe_4]^+[C_6F_{11}O]^-$ as well as to literature values.[8, 9] All C-C-C-angles are in between 110.7(2)° (C2-C1-C6) and 114.7(2)° (C5-C6-C1). The F-C-F angles are ranging from 107.8(2)° (F19-C12-F20) to 108.8(2)° (F16-C10-F15). The CCF-angel are in a range of 108.0(2)° (F19-C12-C11) and 109.6(2)° (F17-C11-C12). The OCO angles are 108.8(2) (O1-C1-O2) and 113.3(2)° (O4-C7-O3). All observed angles are similar to $[NMe_4]^+[C_7F_{13}O]^-$ as well as $[NMe_4]^+[C_6F_{11}O]^-$ and literature values.[8, 9]

The molecules are connected with hydrogen bonds between the Hydrogen and the Oxygen atoms of another molecule with an average length of 2.055 Å. The molecules are forming pillars containing four stacks of molecules hold together with hydrogen bonds (see Figure 4-10). The backbone of the pillars are aggregating in fluorinated domains.

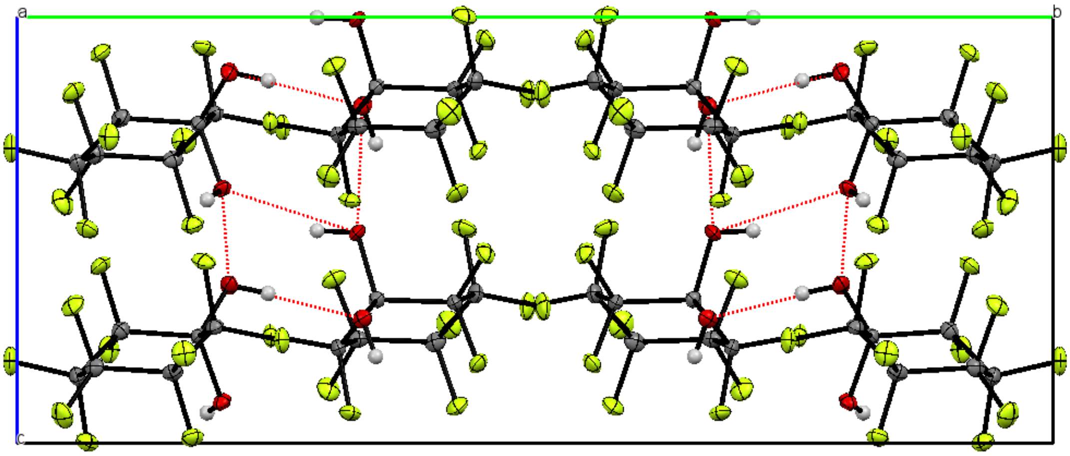


Figure 4-8: Unit cell of $C_6F_{10}(OH)_2$ with view along a.

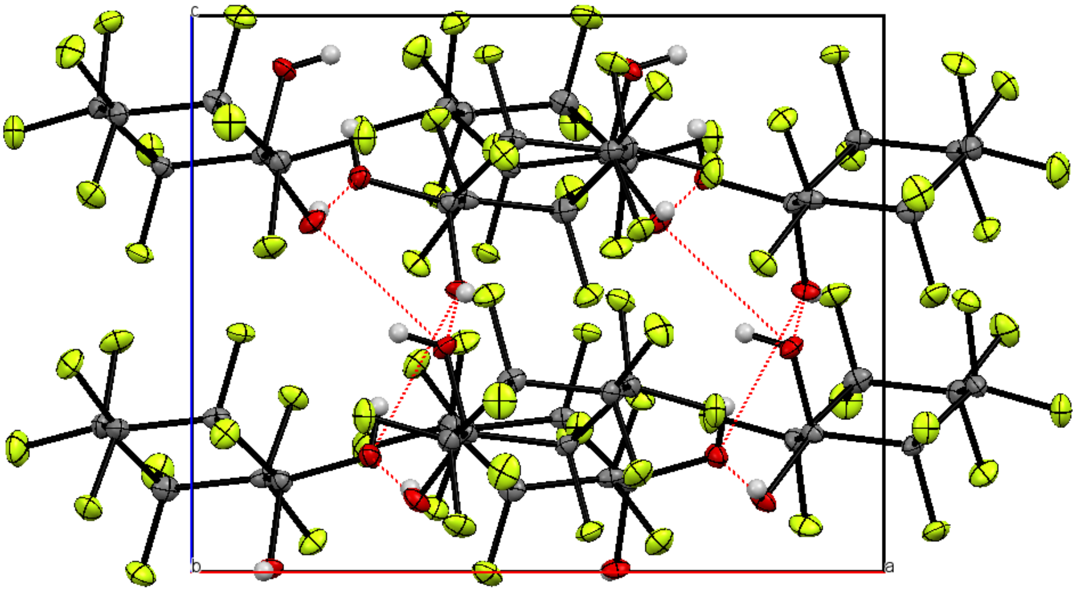


Figure 4-9: Unit cell of $C_6F_{10}(OH)_2$ with view along b.

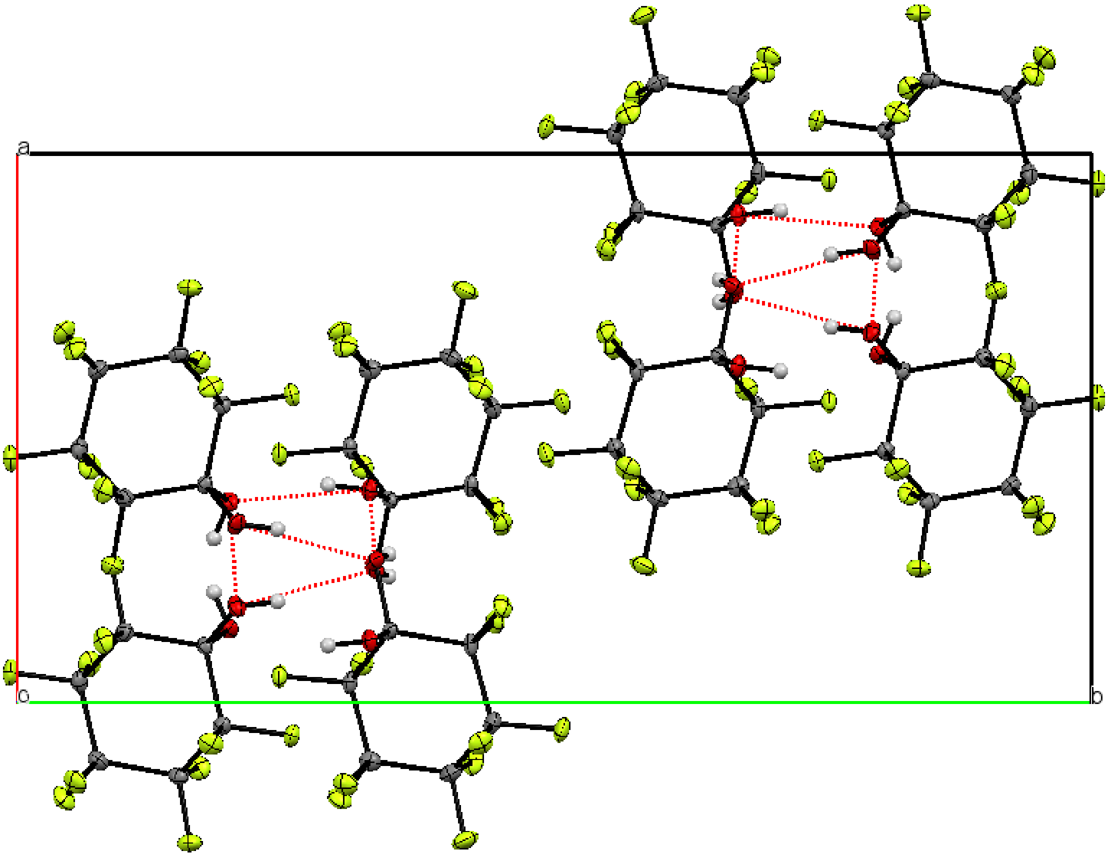


Figure 4-10: Unit cell of $C_6F_{10}(OH)_2$ with view along c.

5. Gas phase electron diffraction

The electron diffraction patterns were recorded on the heavily improved Balzers Eldigraph KD-G2 gas-phase electron diffractometer at Bielefeld University. Experimental details are listed in Table 5-1, instrumental details are reported elsewhere.[18, 19]

Table 5-1: Details of the gas-phase electron diffraction experiment for 1-trifluoromethyl perfluorocyclohexan-1-ol and perfluorocyclohexanol.

	1-trifluoromethylperfluoro-cyclohexan-1-ol (**1**)		perfluorocyclohexan-1,1-diol (**6**)	
Parameters	short detector distance	long detector distance	short detector distance	long detector distance
noozle-to-plate distance, mm	250.0	500.0	250.0	500.0
accelerating voltage, kV	60	60	60	60
fast electron current, μA	1.54	1.54	1.52	1.52
electron wavelength,[a] Å	0.048761	0.048592	0.048654	0.048598
nozzle temperature, K	291	294	298	298
Sample pressure,[b] mbar	1.4×10^{-6}	1.1×10^{-6}	3.6×10^{-6}	2.7×10^{-6}
residual gas pressure[c], mbar	2.0×10^{-7}	2.5×10^{-7}	5.4×10^{-7}	7.2×10^{-7}
exposure time, s	8	10	10	10
used s range, Å^{-1}	5.0 to 31.0	2.1 to 14.0	5.0 to 31.0	2.1 to 14.0
number of inflection points[d]	4	3	3	4
R_f factor	3.315	0.883	3.701	2.380

[a] Determined from CCl_4 diffraction patterns measured in the same experiment.

[b] During the measurement.

[c] Between measurements.

[d] Number of inflection points on the background lines.

The electron diffraction patterns, three for each, long and short nozzle-to-plate distance were measured on the Fuji BAS-IP MP 2025 imaging plates, which were scanned by using calibrated Fuji BAS.1800II scanner. The intensity curves (Figure 5-1 and Figure 5-2) were obtained by applying the method described earlier.[20] Sector function and electron wavelength were refined[21] using carbon tetrachloride diffraction patterns, recorded in the same experiment as the substance under investigation.

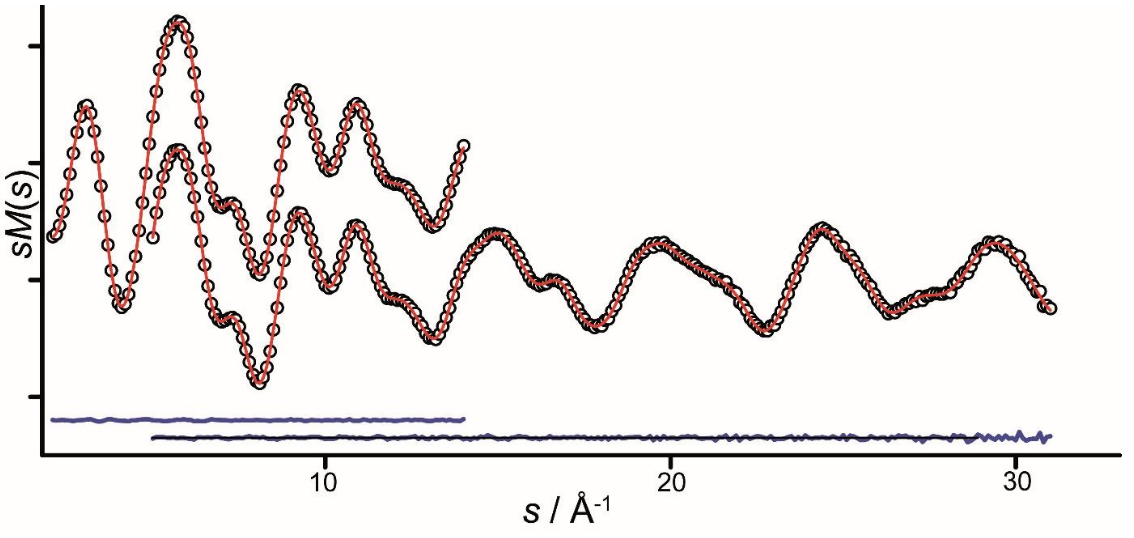


Figure 5-1: Experimental (circles) and model (lines) molecular intensity curves of 1-trifluoromethyl perfluorocyclohexan-1-ol for long and short nozzle-to-plate distance. The respective difference curves are shown at the bottom.

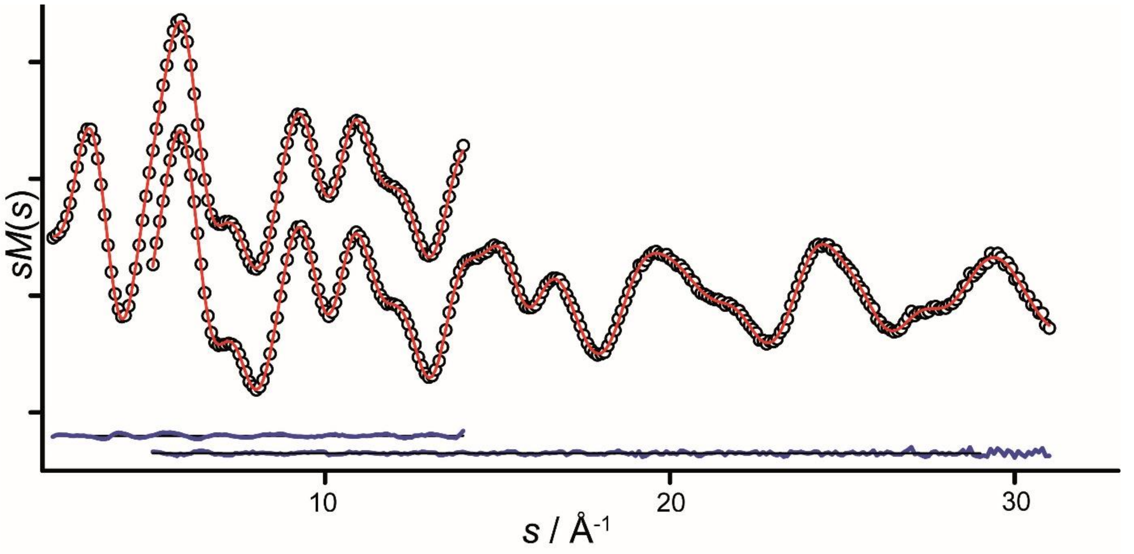


Figure 5-2: Experimental (circles) and model (lines) molecular intensity curves of perfluorocyclohexan-1,1-diol for long and short nozzle-to-plate distance. The respective difference curves are shown at the bottom.

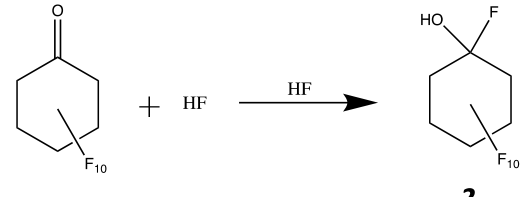
Gas-phase structure analysis

The structural analysis was performed using the UNEX program.[20, 21] All refinements were performed using two intensity curves simultaneously (Figures 5-1 and 5-2), one from the short and another from the long nozzle-to-detector distance. These were obtained by averaging intensity curves measured in independent experiments obtained at the same camera distance. For the structure of both molecules the starting geometry was taken form PBE0/cc-pVTZ calculations was taken. On the same level of theory starting values for the amplitudes of vibration curvilinear corrections were calculated for the gas-phase structure refinement. The groups where the differences are fixed at the computational level can be seen in Table 9-1 and Table 9-4 for the *c*-C_6F_{10}-1-(CF_3)OH and *c*-C_6F_{10}-1,1-$(OH)_2$, respectively. In both cases, the Z-matrix did not obey any symmetry. All experimental and refinement data are listed in the appendix (Table 9-1 to Table 9-8).

6. Undecafluorocyclohexanol (2): $C_6F_{11}OH$

6.1 Synthesis:

Addition of HF to **3** at room temperature to obtain the fluoroalcohol ***2*** (equation {4}). All experiments were done in PFA reaction vessels with a diameter of ½" or ¼", which are closed with a KEL-F valve. Prior synthesis, the vessels were dried using anhydrous HF. First 0.5 mmol **3** was condensed using liquid nitrogen (LN2) at a grease-free glass-vacuum line into a PFA-Vessel. In a second step, an excess of HF (~2 mL) was condensed onto the ketone, using a stainless-steel-vacuum-line. The mixture was warmed up to room temperature and the components were mixed for a few minutes. Afterwards it was cooled down with LN2. The removal of HF occurred at –78°C (dry Ice) in a dynamic vacuum overnight. ***2*** decomposes in a reverse of Eq. {4}. It is stable with inert conditions below −30 °C and under its own vapor pressure, it is stable even at ambient temperature.



3 ***2*** {4}

6.2 Analysis with vibrational spectroscopy

As vibrational analysis IR and Raman spectroscopy was used. The Raman spectrum was measured at –196 °C (77 K) and the IR at –30 °C (243 K) due to instrumental limitations, which can cause a shift of some *cm^{-1}* between the spectra. The experimental data are shown in Figure 6-1 and the assignment was done in Table 4-1. The calculation was done using DFT on def2-TZVPP[16]-level with Turbomole[4, 5]. In addition, the module AORORCE[6, 7] was used to calculate the frequencies on analytical level. The calculations were done for the OH in axial and in equatorial position.

The OH-vibration at 3589 cm^{-1} is a sharp peak in the IR-spectrum. Comparing to ***6***, which observed a broad OH-vibration, which is more a broad signal rather than a sharp one. The other signals are similar to ***6*** and are underlying only slight shifts, which are caused by the different compound. It can be expected, that the difference between **6** and the **2** should be small in vibrational spectroscopy, because fluorine and a hydroxyl group are isoelectronic.

Table 6-1: experimental IR and calculated vibrational data of $C_6F_{11}OH$.

IR	Raman	$C_6F_{11}OH$		assignment
(exp) [cm^{-1}]	(exp) [cm^{-1}]	Equatorial OH (cal.)	Axial OH (cal.)	
3589 (w)	-	3800	3806	υ(OH)
-	2859 (w)	-	-	*
-	2229 (vw)	-	-	*
-	2084 (vw)	-	-	*
-	2029 (vw)	-	-	*

1392 (vw)	1394 (vw)	1363	1368	δ (COH)
-	1330	-	-	*
1312 (m)	1319 (m)	1310	1318	υ_{s} (CC)
1301 (m, sh)	1303 (w, sh)	1299	1301	υ_{as} (CC)
-	-	1295	1295	υ_{as} (CC)
-	-	1288	1281	υ_{as} (CC)
-	1273 (w)	1268	1267	υ_{as} (CO)
1249 (s)	1239 (w)	1243	1241	υ_{as} (CC)
1225 (s)	1205 (vw)	1219	1199	υ_{as} (CC)
1185 (vs)	1181 (vw)	1186	1177	υ_{as}(CF)
-	1168 (vw)	1168	1167	υ_{as}(CF)
-	1163 (vw)	1161	1158	υ_{as}(CF), υ(CO)
1153 (s)	-	1159	1150	υ_{as}(CC)
-	-	1138	1140	υ_{as}(CF)
1119 (m)	1113 (vw)	1102	1133	δ (COH)
-	-	1058	1052	υ_{as}(CF)
1042 (s)	1049 (w)	1053	1049	υ_{as}(CF), υ_{as}(CC)
963 (s, sh)	-	986	980	υ_{as}(CF), δ (CCF)
945 (vs)	-	980	979	υ_{as}(CF), δ (CCF)
851 (m)	-	861	858	δ (CCF)
-	730 (vw)	-	-	*
692 (vw)	697 (vs)	685	690	δ_{s}(FCF), δ(OCF)
676 (w)	680 (vw)	678	676	δ_{as}(FCF), δ(OCF)
-	634 (vw)	631	639	δ_{as}(FCF), δ(OCF)
632 (vs)	-	631	633	δ_{as}(FCF)
599 (w)	601 (w)	599	601	δ_{as}(FCF), δ(OCF)
-	-	596	595	δ_{as}(FCF)
558 (vw)	565 (m)	562	558	δ_{as}(FCF), δ(OCF)
-	538 (w)	-	-	*
-	473 (vw)	475	475	δ_{as}(FCF), δ(OCC)
469 (vs)	-	470	470	Framework vib
415 (vw)	-	412	416	Framework vib
-	386 (m)	369	372	Framework vib
-	374 (m)	367	367	Framework vib
-	342 (s)	335	337	Rocking CF_2
-	333 (m, sh)	331	330	Rocking CF_2
-	325 (w, sh)	329	329	Wagging CF_2
-	310 (vw)	316	313	Wagging CF_2
-	-	306	304	Wagging CF_2
-	-	300	302	Wagging CF_2
-	285 (w)		284	Wagging CF_2
			284	Wagging CF_2

* These vibrations belong to the starting material decafluorocyclohexanon ($C_6F_{10}O$).

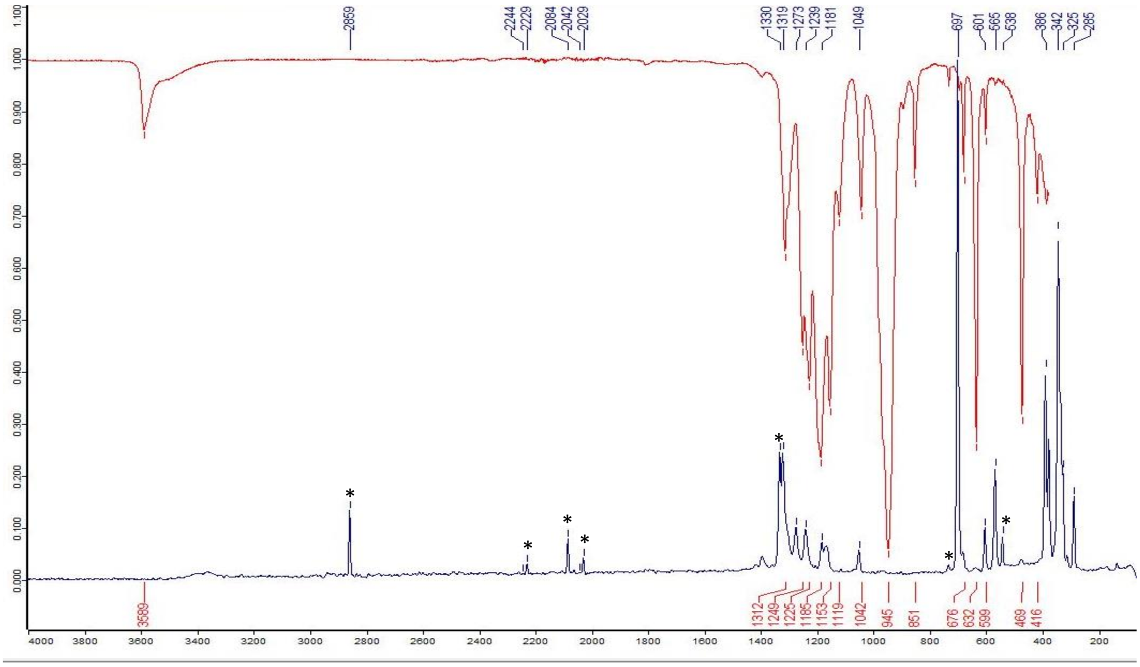
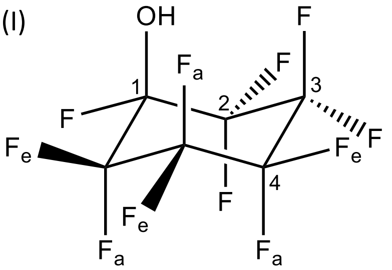
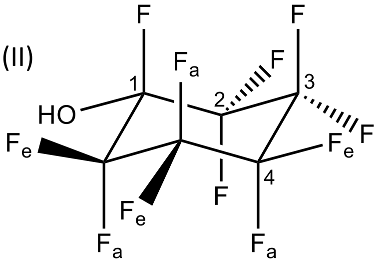


*Figure 6-1: IR and Raman measurements of the product **2**, obtained by HF addition to the ketone **3** (starting material vibrations marked with *). The Raman was measured in vacuum at low temperature. The IR was measured in the glove box, after the sample was cooled to -35°C in the freezer and fast handling afterwards.*

6.3 Analysis with NMR-spectroscopy

The NMR data of the two isomers of ***2*** were obtained in $CFCl_3$ at 223K. In Table 4-12 the assignments of the NMR signals are shown. ^{19}F-shifts are given with respect to $CFCl_3$, ^{1}H and ^{13}C shifts with respect to TMS. In the following figures, the NMR spectra are shown.

*Table 6-2: NMR-shifts of **2** in $CFCl_3$ at 223 K. Assignments according to the schemes on the right. The molar ratio of the products I and II in $CFCl_3$ at 223 K is 2:1.*

	shift [ppm]		**multiplicity**	**assignment**	**Lewis structure of $C_7F_{13}OH$. Numbering Scheme**
	I	**II**			
δ^{19}F	−134.4	−121.6	br	1	(I) 
	−122.6	−121,1	br	2a	
	−122.6	−123.4	br	3a	
	−123.5	−123.5	br	4a	
	−142.4	−142.6	br	2e	
	−141.5	−141.1	br	3e	
	−142.0	−142.0	br	4e	
δ^{1}H	4.74[a]	4.71[a]	s	OH	(II) 
δ^{13}C	100.9	100.9		1	
	109.0	108.3		2	
	107.6	107.7		3	
	107.4	107.4		4	

[a] The ^{1}H spectrum was not calibrated

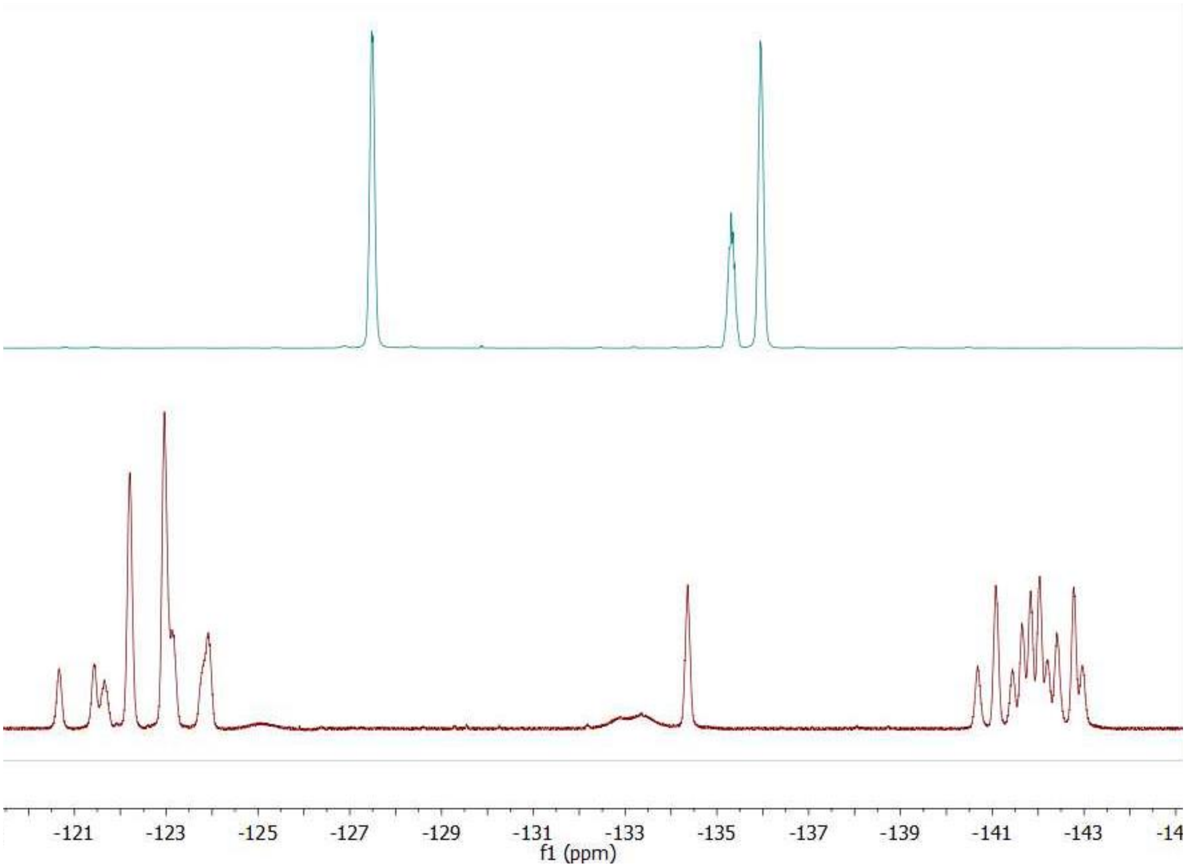


*Figure 6-2: ^{19}F NMR spectra (376.54 MHz) of **2** in $CFCl_3$ at 223 K (red, bottom) and the starting material $C_6F_{10}O$ (282.42 MHz, pure substance) at 298 K (blue, top).*

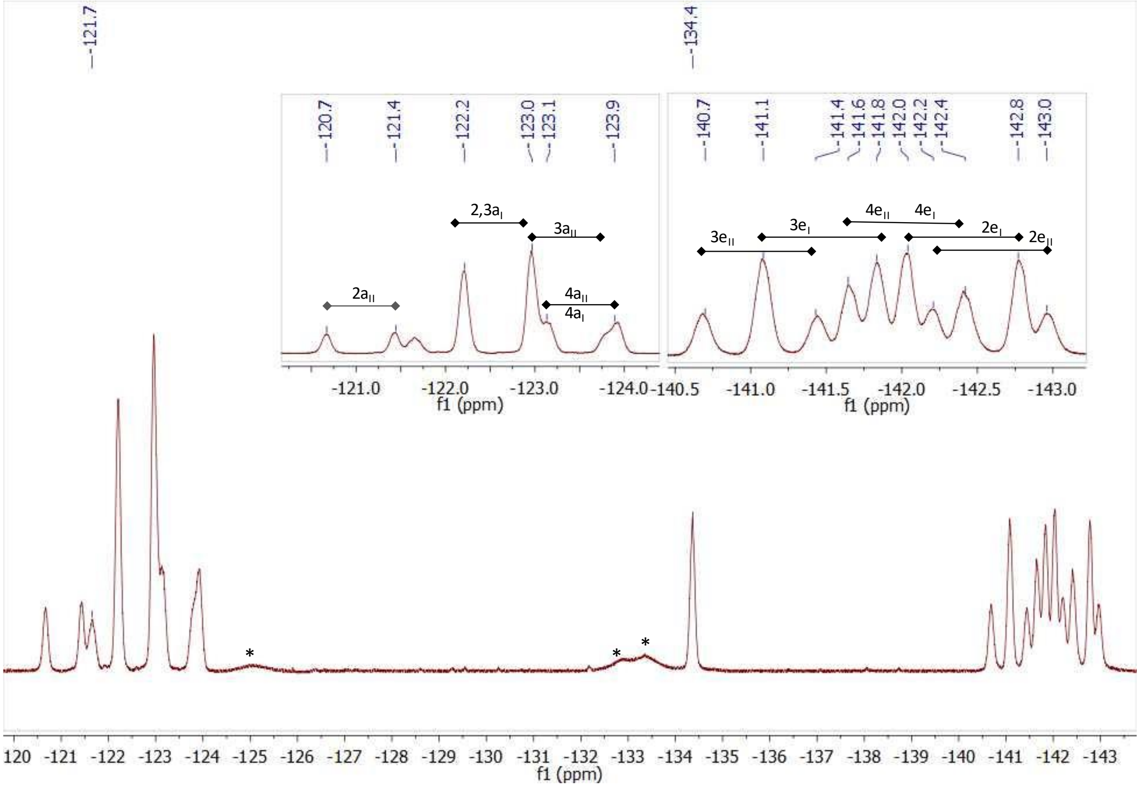


*Figure 6-3: Selected area from the ^{19}F NMR spectrum (376.54) **2** in $CFCl_3$ at 223 K. The detailed spectra insets show the resonances of the axial (left) and the equatorial fluorine atoms (right) together with their assignments. The assignment of the isomers is shown by subscripts (I = axial OH group, II = equatorial OH group). Asterisks mark signals of remnants of **3**.*

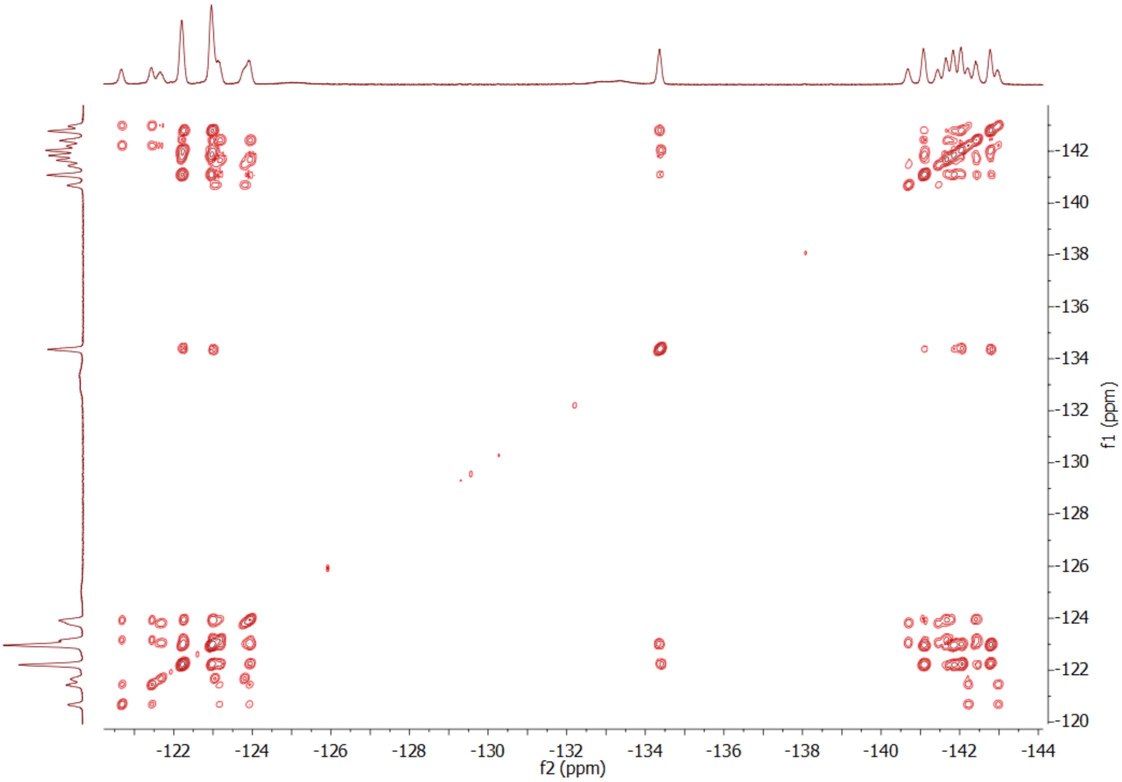


*Figure 6-4: ^{19}F COSY NMR spectrum (376.54 MHz) of **2** in $CFCl_3$ at 223 K.*

The ^{19}F COSY NMR (Figure 4-35) allows the assignment of the positions of the fluorine atoms. Intensive crosspeaks result first of all from the great $^{2}J_{F\text{-}F}$ couplings. Additional crosspeaks are due to formal $^{3}J_{F\text{-}F}$ or $^{4}J_{F\text{-}F}$ couplings. The absolute value of these couplings grows larger, when the coupling fluorine atoms are pointing to one another leading to more intensive crosspeaks between the signals of such fluorine atoms. This indicates that there are substantial contributions of through-space interactions to these formal $^{3}J_{F\text{-}F}$ and $^{4}J_{F\text{-}F}$ couplings. Furthermore, the fact that there is a crosspeak between the fluorine resonance of 1_{II} at −121.6 ppm and the fluorine signal of $3a_{II}$ and no correlation of the signal of 1_{II} to the resonance of $2a_{II}$ allows to identify this molecule as isomer II.

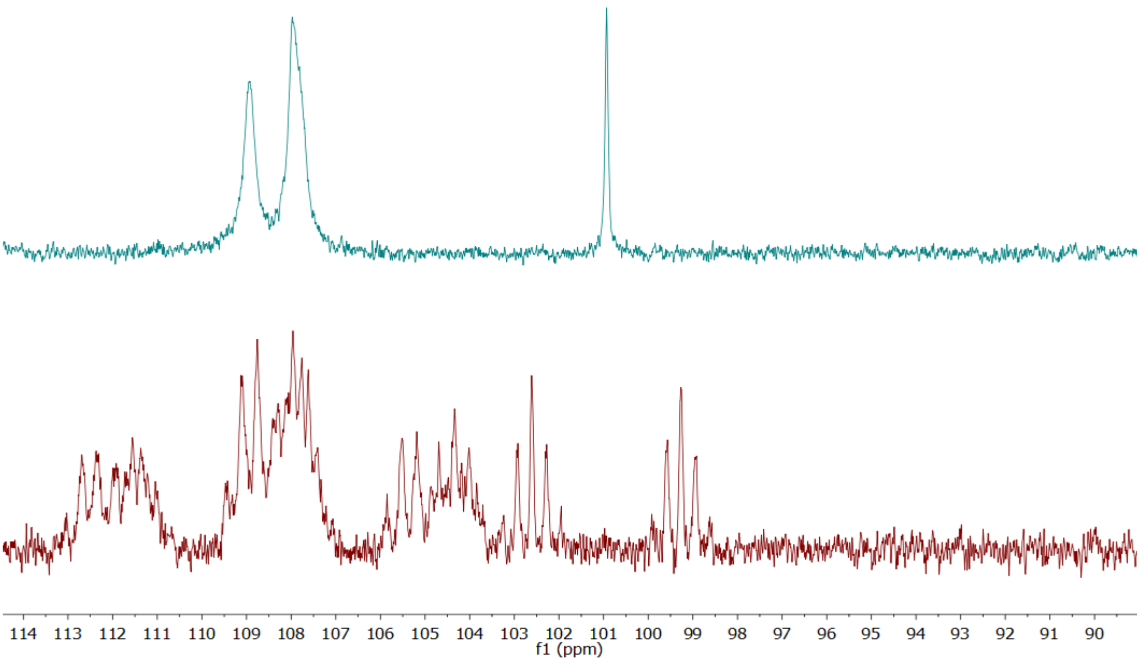


*Figure 6-5: ^{13}C NMR spectra (75.48 MHz) of **2** in CFCl$_3$ at 298 K. The upper spectrum is ^{19}F decoupled and the lower spectrum is not decoupled. The signal at 100.9 ppm shows a doublet splitting of 253 Hz. Thus, only one fluorine atom is directly attached to this carbon atom. The other signals in this area show a triplet splitting with $^1J_{F\text{-}C}$ couplings and hence belong to CF$_2$ groups.*

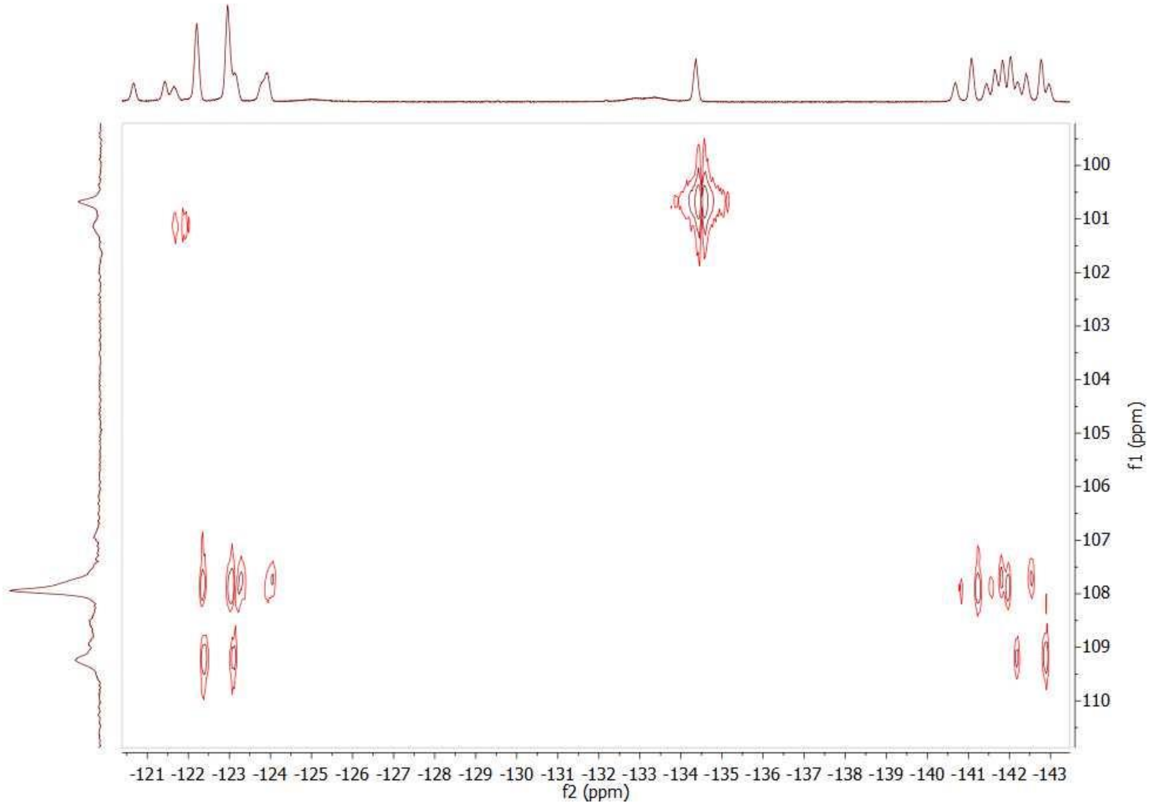


*Figure 6-6: ^{19}F,^{13}C HSQC NMR spectrum (376.54 MHz, optimized for $^1J_{F\text{-}C}$ couplings) of **2** in CFCl$_3$ at 223 K.*

In the ^{1}J ^{19}F,^{13}C correlation in Figure 4-37 it is easy to identify which fluorine atoms are attached to the same carbon atom. As for C$_7$F$_{13}$OH and ***6*** in **2** the carbon atom in position 2 shows the farthest downfield shift of the CF$_2$ groups in the perfluorocyclohexyl ring.

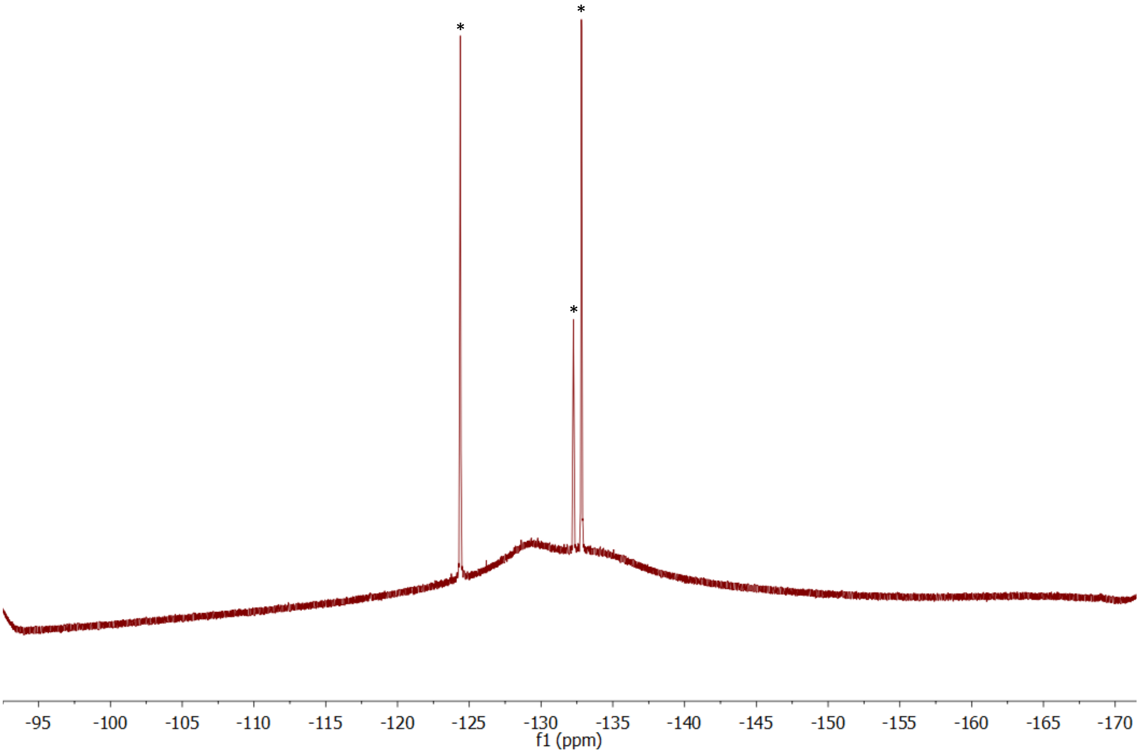


*Figure 6-7: ^{19}F NMR spectrum (376.54 MHz) of **2** in $CFCl_3$ at 298 K. Asterisks mark signals of remnants of **3**.*

In the ^{19}F NMR spectrum of **2** in $CFCl_3$ at ambient temperature (Figure 4-38) only two very broad and overlapping coalescence signals are detected for the fluorine atoms of **2**. The fluorine atoms of **2** must exchange so fast, that both isomers cannot be distinguished anymore on the NMR timescale and only one broad signal is found for axial and equatorial positions respectively. In contrast, the resonances of remnants of **3** in the sample have grown sharper compared to the measurement at 223 K. Therefore, the exchange must be chiefly due to the folding of the six membered ring. Elimination and addition of HF can only play a minor role if any at all in this exchange process of **2** in $CFCl_3$ solution for otherwise individual resonances of ***3*** as inevitable intermediate of such an intermolecular exchange would not be detected.

6.4 Attempts to obtain a crystal structure

To obtain crystals, it was tried to crystallize out of HF, $CFCl_3$, ortho-difluorobenzene and $CHFCl_2$. The used temperatures were: −78 °C, −48 °C, −30 °C, −20 °C, −10 °C and 0 °C. However, none of these methods succeeded.

6.5 Gas-phase IR

The Gas-Phase IR spectra of the vapour of $C_6F_{11}OH$ will be compared to the solid-state IR of $C_6F_{11}OH$ and to the Gas-Phase IR of $C_6F_{10}O$ (starting material). The CO-vibration at 1808 cm^{-1} is visible significant and according to $C_6F_{10}O$. A OH-vibration is present at 3628 and 3589 cm^{-1}. In the solid-state-IR of $C_6F_{11}OH$ is only one vibration at 3589 cm^{-1} with a significantly higher intensity visible. These both vibrations were also detected in the starting material, which could be an impurity.

Comparing the finger-print area, shows an unambiguous result: The finger print is perfect matching to the starting material and only a rare coincidence to the solid state spectra of $C_6F_{11}OH$.

Summarizing the solid $C_6F_{11}OH$ has a vapour pressure, which is depending on the temperature. The vapour pressure at room temperature is higher than on 0 °C. The gas-IR spectra clearly show that $C_6F_{11}OH$ is decomposing to $C_6F_{10}O$ and HF. HF is not visible in the gas-IR, because it will stick to the stainless steel line and react with the glass of the cell or the tube, which was used for transferring the gas into the gas-IR-cell.

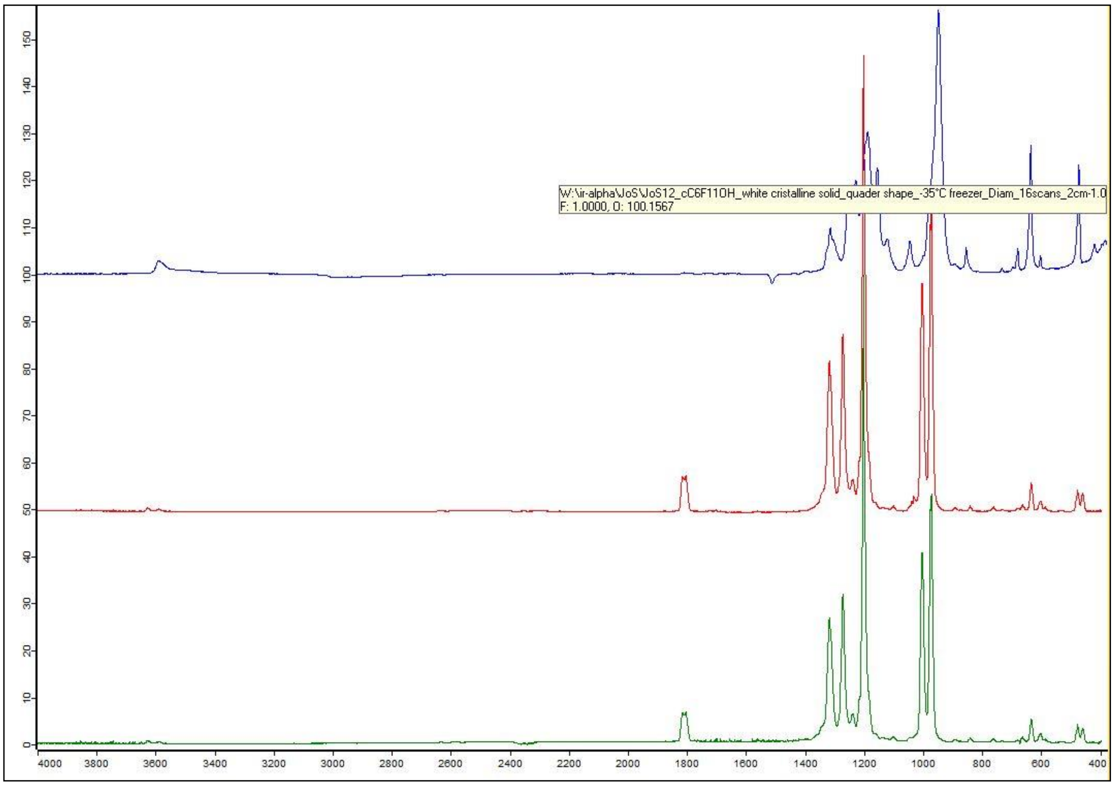


Figure 6-8: Gas-Phase IR of the vapour of $C_6F_{11}OH$ at room temperature with 15 mbar pressure (red, middle spectrum). As comparison, a $C_6F_{10}O$ gas-IR with 10 mbar pressure (green, bottom) and $C_6F_{11}OH$ solid-IR (blue, top) are shown.

7. Analytical methods

7.1 NMR spectrometry

All measurements were done on a Bruker Avance II$^+$ 400 MHz WB with a BBFO probe head, Bruker Avance IIIHD 300 MHz with BBFO probe head and Bruker 200 MHz with QNP probe head. The low Temperature measurements were done at the Bruker Avance II$^+$ 400 MHz. For measurements the Software Topspin version 3.2 and for analysis MestReNova Version 12.0 were used.

7.2 IR-spectroscopy

As instrument, a Bruker Alpha-P IR spectrometer equipped with a Platinum-ATR with a diamond crystal was used to gather spectra in Argon atmosphere (glove box). To measure gas-IR a Nicolet Magna IR spectrometer for FIR (250-600cm^{-1}) and MIR (400-4000 cm^{-1}) measurements was used. The evaluation ensued using OPUS software.

7.3 Raman-spectroscopy

As instrument, a Bruker Vertex 70 Raman spectrometer was used for Raman-spectra acquiring. A special low temperature unit allowed measurements at −196 °C. The evaluation ensued using OPUS software.

7.4 Single crystal X-ray diffractometer

All crystal structures were obtained at 100 K using a Bruker Smart APEX II QUAZAR single-crystal diffractometer with Oxford Cryosystems 800 crystal cooling device. As X-ray Mo-Kα with $\lambda = 0.7107$ Å was used.

7.5 Gas phase electron diffraction

The electron diffraction patterns were recorded on the heavily improved Balzers Eldigraph KD-G2 gas-phase electron diffractometer at Bielefeld University. Experimental details are listed in Table S4, instrumental details are reported elsewhere.[18, 19]

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9. Appendix to the Gas Phase Electron Diffraction

***Table 9-1**. Z-Matrix used in the refinement of the gas-phase structure of 1-trifluoromethyl perfluorocyclohexan-1-ol. Distances r are given in Å, angles a and dihedrals d are given in °. The numbers written in line with the parameter indicate the groups they were refined in.*

```
 1 C
 2 C   1    rcc1
 3 F   2    rcf1  1   accf1
 4 F   2    rcf2  1   accf2  3   afcf1  1
 5 F   2    rcf3  1   accf3  3   afcf2 -1
 6 O   1     rco  2    acco  3   dfcco
 7 H   6     roh  1    acoh  2   dccoh
 8 C   1    rcc2  2   accc1  6   aocc1 -1
 9 C   1    rcc3  2   accc2  6   aocc2  1
10 C   8    rcc4  1   accc3  2  dcccc1
11 C   9    rcc5  1   accc4  2  dcccc2
12 C  10    rcc6 11    rcc7  8   fcccc  4
13 F   8    rcf4  1   accf4  2  dcccf1
14 F   8    rcf5  1   accf5  6  doccf1
15 F   9    rcf6  1   accf6  2  dcccf2
16 F   9    rcf7  1   accf7  6  doccf2
17 F  10    rcf8  8   accf8 13  dfccf1
18 F  10    rcf9  8   accf9 14  dfccf2
19 F  11   rcf10  9  accf10 15  dfccf3
20 F  11   rcf11  9  accf11 16  dfccf4
21 F  12   rcf12 10  accf12 11  accf14 -1
22 F  12   rcf13 10  accf13 11  accf15  1

Variables:
  rcc1       1.55252964         1
  rcf1       1.32275110         2
  rcf2       1.32475110         2
  rcf3       1.34255110         2
   rco       1.41277805         2
   roh       0.97485858         4
  rcc2       1.54782964         1
  rcc3       1.55432964         1
  rcc4       1.54362964         1
  rcc5       1.54182964         1
  rcc6       1.53392964         1
  rcc7       1.53282964         1
  rcf4       1.33275110         2
  rcf5       1.35065110         2
  rcf6       1.35035110         2
  rcf7       1.34125110         2
  rcf8       1.33745110         2
  rcf9       1.33875110         2
 rcf10       1.33605110         2
 rcf11       1.34275110         2
 rcf12       1.33385110         2
 rcf13       1.34445110         2
 accf1     111.50195008         5
 accf2     107.92785008         5
 afcf1     109.27430592         6
 accf3     105.12575008         5
 afcf2     108.98740592         6
  acco     109.98570683        11
  acoh     111.89233276        12
 accc1     112.25056862         8
 aocc1     100.66300126         7
 accc2     112.06976862         8
 aocc2     108.99126568         9
 accc3     115.58469845         9
 accc4     112.44658628        10
 accf4     111.57236814        10
 accf5     109.11286814        10
 accf6     108.91276814        10
 accf7     112.53056814        10
 accf8     109.29576814        10
 accf9     110.31816814        10
accf10     109.62716814        10
accf11     109.93766814        10
accf12     110.59996814        10
accf14     110.44347814        10
accf13     109.25636814        10
accf15     108.90766814        10
 dfcco    -177.51263760        15
 dccoh      62.12155253        16
dcccc1    -175.96796692        17
dcccc2     172.67539533        18
 fcccc    -129.06024475        13
dcccf1      65.03561885        14
doccf1    -169.99307230        13
dcccf2     -64.97378115        14
doccf2     173.92682770        13
```

```
dfccf1     -65.28328115        14
dfccf2     168.99592770        13
dfccf3      68.81791885        14
dfccf4    -163.46127230        13
```

Table 9-2: *Cartesian coordinates for the refined structure of 1-trifluoromethyl perfluorocyclohexan-1-ol.*

```
------------------------------------------------------------------------------
N | At | An |    Mass    |        X        |        Y        |         Z
-------------------------------------------------------------------------------
 1  C     6   12.00000000   -1.005879296322    0.003220744171    0.355437262954
 2  C     6   12.00000000   -2.491025266689    0.033013087318   -0.096007234309
 3  F     9   18.99840320   -2.604525794576   -0.145431848390   -1.401742849907
 4  F     9   18.99840320   -3.128838736852   -0.941290265054    0.535572073438
 5  F     9   18.99840320   -2.927475999320    1.263641441690    0.216255567780
 6  O     8   15.99491462   -0.925114125458    0.139375277866    1.759317862659
 7  H     1    1.00782503   -1.366145864709   -0.596749829921    2.221876055444
 8  C     6   12.00000000   -0.229612244116    1.262643743012   -0.099578952343
 9  C     6   12.00000000   -0.293331131275   -1.311975917620   -0.067023943675
10  C     6   12.00000000    1.279606564033    1.268750838423    0.224479292587
11  C     6   12.00000000    1.222045635590   -1.277387432279    0.215244577467
12  C     6   12.00000000    1.916203398987   -0.018080735598   -0.315658743919
13  F     9   18.99840320   -0.697558246637    2.364767660944    0.485720025041
14  F     9   18.99840320   -0.388450795235    1.422947422943   -1.431243860946
15  F     9   18.99840320   -0.863893963023   -2.347776675984    0.584913881020
16  F     9   18.99840320   -0.439492928577   -1.578954007804   -1.373283462947
17  F     9   18.99840320    1.855843645539    2.317017570278   -0.373737323503
18  F     9   18.99840320    1.470781477979    1.352175741037    1.546881249533
19  F     9   18.99840320    1.811314264060   -2.324728944405   -0.368596815716
20  F     9   18.99840320    1.444164918356   -1.375553616358    1.535853123226
21  F     9   18.99840320    3.219617561229   -0.050824708977   -0.034237172310
22  F     9   18.99840320    1.848452676582   -0.016525814472   -1.658400778774
-------------------------------------------------------------------------------
Rotational constants (MHz):     488.30737183      337.08446441      271.33123605
```

Table 9-3: *Full listing of structural parameters of 1-trifluoromethyl perfluorocyclohexan-1-ol. r_a, r_g, r_e values are given in Å. Errors correspond to one time standard deviation. For atom numbering, see Table S5.*

```
-------------------------------------------------------------------
 No.  Type      i    j    k    l    a-Value  g-Value  c-Value    Error
--------------------------------------------------------------------
   1 stretch    1    2    0    0    1.56433  1.56614  1.55253  0.00035
   2 stretch    1    6    0    0    1.41978  1.42131  1.41278  0.00012
   3 stretch    1    8    0    0    1.55853  1.56031  1.54783  0.00035
   4 stretch    1    9    0    0    1.56423  1.56608  1.55433  0.00035
   5 stretch    2    3    0    0    1.32885  1.33035  1.32275  0.00012
   6 stretch    2    4    0    0    1.33125  1.33275  1.32475  0.00012
   7 stretch    2    5    0    0    1.34825  1.34982  1.34255  0.00012
   8 stretch    6    7    0    0    0.98966  0.99458  0.97486  0.00434
   9 stretch    8   10    0    0    1.55343  1.55518  1.54363  0.00035
  10 stretch    8   13    0    0    1.33925  1.34073  1.33275  0.00012
  11 stretch    8   14    0    0    1.35625  1.35777  1.35065  0.00012
  12 stretch    9   11    0    0    1.55163  1.55337  1.54183  0.00035
  13 stretch    9   15    0    0    1.35665  1.35818  1.35035  0.00012
  14 stretch    9   16    0    0    1.34725  1.34876  1.34125  0.00012
  15 stretch   10   12    0    0    1.54413  1.54585  1.53393  0.00035
  16 stretch   10   17    0    0    1.34375  1.34523  1.33745  0.00012
  17 stretch   10   18    0    0    1.34485  1.34634  1.33875  0.00012
  18 stretch   11   12    0    0    1.54303  1.54474  1.53283  0.00035
  19 stretch   11   19    0    0    1.34215  1.34363  1.33605  0.00012
  20 stretch   11   20    0    0    1.34925  1.35075  1.34275  0.00012
  21 stretch   12   21    0    0    1.34025  1.34172  1.33385  0.00012
  22 stretch   12   22    0    0    1.35035  1.35186  1.34445  0.00012
  23 bend       2    1    6    0                     109.98571  0.33494
  24 bend       2    1    8    0                     112.25057  0.10437
  25 bend       2    1    9    0                     112.06977  0.10437
  26 bend       1    2    3    0                     111.50195  0.12138
  27 bend       1    2    4    0                     107.92785  0.12138
  28 bend       1    2    5    0                     105.12575  0.12138
  29 bend       6    1    8    0                     100.66300  0.33254
  30 bend       6    1    9    0                     108.99127  0.24409
  31 bend       1    6    7    0                     111.89233  0.34862
  32 bend       8    1    9    0                     112.25174  0.22116
  33 bend       1    8   10    0                     115.58470  0.24409
  34 bend       1    8   13    0                     111.57237  0.06259
  35 bend       1    8   14    0                     109.11287  0.06259
  36 bend       1    9   11    0                     112.44659  0.06259
  37 bend       1    9   15    0                     108.91277  0.06259
  38 bend       1    9   16    0                     112.53057  0.06259
  39 bend       3    2    4    0                     109.27431  0.24591
  40 bend       3    2    5    0                     108.98741  0.24591
  41 bend       4    2    5    0                     114.00044  0.45313
  42 bend      10    8   13    0                     104.34848  0.32073
  43 bend      10    8   14    0                     108.75317  0.51918
  44 bend       8   10   12    0                     109.17879  0.27476
  45 bend       8   10   17    0                     109.29577  0.06259
```

```
 46 bend       8   10   18    0                      110.31817   0.06259
 47 bend      13    8   14    0                      107.07080   0.33510
 48 bend      11    9   15    0                      110.12695   0.31108
 49 bend      11    9   16    0                      106.85003   0.62475
 50 bend       9   11   12    0                      113.58521   0.28577
 51 bend       9   11   19    0                      109.62717   0.06259
 52 bend       9   11   20    0                      109.93767   0.06259
 53 bend      15    9   16    0                      105.75156   0.47155
 54 bend      12   10   17    0                      108.73648   0.47601
 55 bend      12   10   18    0                      109.92806   0.20814
 56 bend      10   12   11    0                      112.29101   0.26576
 57 bend      10   12   21    0                      110.59997   0.06259
 58 bend      10   12   22    0                      109.25637   0.06259
 59 bend      17   10   18    0                      109.35692   0.42417
 60 bend      12   11   19    0                      107.03383   0.36160
 61 bend      12   11   20    0                      109.01365   0.42753
 62 bend      11   12   21    0                      110.44348   0.06259
 63 bend      11   12   22    0                      108.90767   0.06259
 64 bend      19   11   20    0                      107.42845   0.47474
 65 bend      21   12   22    0                      105.06931   0.37390
 66 torsion    3    2    1    6                     -177.51264   0.35694
 67 torsion    4    2    1    6                      -57.49004   0.41766
 68 torsion    5    2    1    6                       64.53527   0.46204
 69 torsion    2    1    6    7                       62.12155   0.34999
 70 torsion    3    2    1    8                       71.29364   0.37490
 71 torsion    4    2    1    8                     -168.68376   0.39380
 72 torsion    5    2    1    8                      -46.65846   0.50575
 73 torsion    2    1    8   10                     -175.96797   0.45658
 74 torsion    2    1    8   13                       65.03562   0.20013
 75 torsion    2    1    8   14                      -53.06939   0.29644
 76 torsion    3    2    1    9                      -56.10581   0.41239
 77 torsion    4    2    1    9                       63.91679   0.47165
 78 torsion    5    2    1    9                     -174.05791   0.49744
 79 torsion    2    1    9   11                      172.67540   0.45037
 80 torsion    2    1    9   15                      -64.97378   0.20013
 81 torsion    2    1    9   16                       51.95000   0.54935
 82 torsion    7    6    1    8                     -179.29236   0.35756
 83 torsion    6    1    8   10                       67.10835   0.57189
 84 torsion    6    1    8   13                      -51.88807   0.37198
 85 torsion    6    1    8   14                     -169.99307   0.20985
 86 torsion    7    6    1    9                      -61.10794   0.45511
 87 torsion    6    1    9   11                      -65.34777   0.66338
 88 torsion    6    1    9   15                       57.00305   0.43190
 89 torsion    6    1    9   16                      173.92683   0.20985
 90 torsion   10    8    1    9                      -48.66563   0.43304
 91 torsion   13    8    1    9                     -167.66204   0.35383
 92 torsion   14    8    1    9                       74.23295   0.33032
 93 torsion    8    1    9   11                       45.27657   0.38596
 94 torsion    8    1    9   15                      167.62739   0.25408
 95 torsion    8    1    9   16                      -75.44883   0.54051
 96 torsion    1    8   10   12                       52.98854   0.45390
 97 torsion    1    8   10   17                      171.81183   0.38226
 98 torsion    1    8   10   18                      -67.91545   0.44047
 99 torsion    1    9   11   12                      -49.84710   0.46657
100 torsion    1    9   11   19                     -169.51995   0.33350
101 torsion    1    9   11   20                       72.59989   0.61618
102 torsion   12   10    8   13                      175.89342   0.42243
103 torsion   17   10    8   13                      -65.28328   0.20013
104 torsion   18   10    8   13                       54.98943   0.37927
105 torsion   12   10    8   14                      -70.10008   0.25631
106 torsion   17   10    8   14                       48.72321   0.42819
107 torsion   18   10    8   14                      168.99593   0.20985
108 torsion    8   10   12   11                      -55.26711   0.22745
109 torsion    8   10   12   21                     -179.14107   0.26636
110 torsion    8   10   12   22                       65.67567   0.33873
111 torsion   12   11    9   15                     -171.50924   0.43197
112 torsion   19   11    9   15                       68.81792   0.20013
113 torsion   20   11    9   15                      -49.06225   0.51888
114 torsion   12   11    9   16                       74.09174   0.39507
115 torsion   19   11    9   16                      -45.58110   0.45306
116 torsion   20   11    9   16                     -163.46127   0.20985
117 torsion    9   11   12   10                       55.82139   0.31560
118 torsion    9   11   12   21                      179.78247   0.42964
119 torsion    9   11   12   22                      -65.32180   0.32056
120 torsion   11   12   10   17                     -174.43818   0.36443
121 torsion   21   12   10   17                       61.68785   0.43784
122 torsion   22   12   10   17                      -53.49541   0.39886
123 torsion   11   12   10   18                       65.87456   0.30163
124 torsion   21   12   10   18                      -57.99940   0.38855
125 torsion   22   12   10   18                     -173.18267   0.34411
126 torsion   10   12   11   19                      176.95858   0.20384
127 torsion   10   12   11   20                      -67.13457   0.28348
128 torsion   21   12   11   19                      -59.08035   0.28204
129 torsion   22   12   11   19                       55.81539   0.29651
130 torsion   21   12   11   20                       56.82651   0.41012
131 torsion   22   12   11   20                      171.72224   0.28512
```

Table 9-4: *Full listing of interatomic distances, refined vibrational amplitudes l and corrections of 1-trifluoromethyl perfluorocyclohexan-1-ol, all is given in Å. The numbers at the Gu column indicate the groups the amplitudes were refined in.*

At1	At2	r_a	l	corr	a	Gr	Gu
O6	H7	0.989659	0.069801	-0.014800	0.000000	0	100
C2	F3	1.328851	0.044649	-0.006100	0.000000	0	101
C2	F4	1.331251	0.044649	-0.006500	0.000000	0	101
C8	F13	1.339251	0.044457	-0.006500	0.000000	0	101
C12	F21	1.340251	0.044361	-0.006400	0.000000	0	101
C11	F19	1.342151	0.044553	-0.006100	0.000000	0	101
C10	F17	1.343751	0.044649	-0.006300	0.000000	0	101
C10	F18	1.344851	0.044745	-0.006100	0.000000	0	101
C9	F16	1.347251	0.045034	-0.006000	0.000000	0	101
C2	F5	1.348251	0.045996	-0.005700	0.000000	0	101
C11	F20	1.349251	0.045034	-0.006500	0.000000	0	101
C12	F22	1.350351	0.045130	-0.005900	0.000000	0	101
C8	F14	1.356251	0.045419	-0.005600	0.000000	0	101
C9	F15	1.356651	0.045612	-0.006300	0.000000	0	101
C1	O6	1.419778	0.046574	-0.007000	0.000000	0	101
C11	C12	1.543030	0.051435	-0.010200	0.000000	0	102
C10	C12	1.544130	0.051535	-0.010200	0.000000	0	102
C9	C11	1.551630	0.052035	-0.009800	0.000000	0	102
C8	C10	1.553430	0.052134	-0.009800	0.000000	0	102
C1	C8	1.558530	0.052634	-0.010700	0.000000	0	102
C1	C9	1.564230	0.053832	-0.009900	0.000000	0	102
C1	C2	1.564330	0.053233	-0.011800	0.000000	0	102
C1	H7	2.011126	0.097338	-0.017800	0.000000	0	103
F21	F22	2.131936	0.061036	-0.006100	0.000000	0	103
F15	F16	2.152699	0.061534	-0.006600	0.000000	0	103
F13	F14	2.163883	0.061135	-0.005800	0.000000	0	103
F19	F20	2.165620	0.060736	-0.006300	0.000000	0	103
F3	F4	2.166547	0.059440	-0.007500	0.000000	0	103
F3	F5	2.175624	0.060338	-0.005900	0.000000	0	103
F17	F18	2.189368	0.060637	-0.005800	0.000000	0	103
F4	F5	2.244614	0.059939	-0.007600	0.000000	0	103
C10	F13	2.288071	0.068730	-0.012400	0.000000	0	104
O6	C8	2.292260	0.071256	-0.011700	0.000000	0	104
C1	F5	2.319496	0.070099	-0.017200	0.000000	0	104
C12	F19	2.321539	0.069678	-0.011900	0.000000	0	104
C11	F16	2.330221	0.070941	-0.011800	0.000000	0	104
C1	F4	2.344359	0.071362	-0.013800	0.000000	0	104
C12	F17	2.348400	0.069572	-0.011800	0.000000	0	104
C11	F22	2.355452	0.071046	-0.011800	0.000000	0	104
C12	F20	2.355953	0.071467	-0.012100	0.000000	0	104
C10	F22	2.361530	0.070941	-0.011900	0.000000	0	104
C8	F17	2.365269	0.069888	-0.012400	0.000000	0	104
C10	F14	2.366337	0.071467	-0.011000	0.000000	0	104
C12	F18	2.366895	0.071046	-0.012100	0.000000	0	104
C9	F19	2.367626	0.069678	-0.012600	0.000000	0	104
C11	F21	2.368827	0.069783	-0.011500	0.000000	0	104
C10	F21	2.372178	0.069783	-0.011700	0.000000	0	104
C9	F20	2.375973	0.071362	-0.011200	0.000000	0	104
C1	F15	2.379534	0.069783	-0.013100	0.000000	0	104
C8	F18	2.380483	0.071677	-0.011900	0.000000	0	104
C1	F14	2.380722	0.071362	-0.016600	0.000000	0	104
C11	F15	2.385506	0.069572	-0.012000	0.000000	0	104
C1	F3	2.393321	0.073256	-0.013100	0.000000	0	104
C1	F13	2.396250	0.069467	-0.011100	0.000000	0	104
C1	F16	2.422222	0.072835	-0.011300	0.000000	0	104
O6	C9	2.430136	0.072098	-0.013300	0.000000	0	104
C2	O6	2.445549	0.070625	-0.015400	0.000000	0	104
F4	H7	2.469918	0.256818	-0.006300	0.000000	0	104
H7	F15	2.484281	0.247556	-0.035200	0.000000	0	104
F5	F13	2.509024	0.116359	-0.007500	0.000000	0	105
C8	C12	2.524280	0.063068	-0.016000	0.000000	0	105
C10	C11	2.564706	0.063068	-0.017900	0.000000	0	105
O6	F13	2.583041	0.111665	-0.008900	0.000000	0	105
F16	F19	2.586810	0.106287	-0.011600	0.000000	0	105
C1	C11	2.588470	0.062775	-0.014900	0.000000	0	105
C9	C12	2.589053	0.063264	-0.016500	0.000000	0	105
C8	C9	2.590814	0.064926	-0.015200	0.000000	0	105
C2	C8	2.591700	0.064437	-0.017600	0.000000	0	105
C2	C9	2.593061	0.063459	-0.016300	0.000000	0	105
F3	F16	2.621660	0.142173	-0.024900	0.000000	0	105
F13	F18	2.626143	0.112447	-0.008300	0.000000	0	105
C1	C10	2.630253	0.062384	-0.014500	0.000000	0	105
F14	F17	2.645546	0.107656	-0.008400	0.000000	0	105
F19	F22	2.650586	0.110981	-0.006200	0.000000	0	105
H7	C9	2.651379	0.169551	-0.024300	0.000000	0	105
F17	F22	2.670502	0.111470	-0.006700	0.000000	0	105
C2	H7	2.673470	0.170040	-0.021200	0.000000	0	105
F4	F15	2.680473	0.100323	-0.013900	0.000000	0	105
F15	F20	2.686825	0.113230	-0.007900	0.000000	0	105
F14	F22	2.696723	0.166520	-0.027000	0.000000	0	105
O6	F18	2.705558	0.152048	-0.011800	0.000000	0	105
F13	F17	2.710889	0.103158	-0.016300	0.000000	0	105

```
F19   F21  2.711206    0.104429   -0.015700   0.000000       0     105
F20   F21  2.720802    0.111567   -0.005600   0.000000       0     105
F5   C8    2.731988    0.069815   -0.015700   0.000000       0     105
F3   F14   2.745982    0.182165   -0.030900   0.000000       0     105
F18   F21  2.750197    0.110589   -0.006700   0.000000       0     105
F18   F20  2.757882    0.176004   -0.030000   0.000000       0     105
F4   O6    2.761089    0.139435   -0.018500   0.000000       0     105
O6   F15   2.767163    0.114892   -0.016000   0.000000       0     105
F17   F21  2.768710    0.104918   -0.015200   0.000000       0     105
F5   O6    2.783771    0.133372   -0.017100   0.000000       0     105
F16   F22  2.812969    0.173018   -0.027800   0.000000       0     106
O6   F20   2.838269    0.154573   -0.017200   0.000000       0     106
F15   F19  2.854950    0.106357   -0.014800   0.000000       0     106
C2   F14   2.872496    0.109765   -0.020200   0.000000       0     106
C8   F22   2.917309    0.110166   -0.021700   0.000000       0     106
C2   F16   2.919037    0.104853   -0.014100   0.000000       0     106
O6   C10   2.924406    0.107961   -0.010300   0.000000       0     106
F3   C9    2.924817    0.126506   -0.012100   0.000000       0     106
F4   C9    2.935336    0.069368   -0.012900   0.000000       0     106
C12   F14  2.957316    0.111670   -0.019200   0.000000       0     106
C8   C11   2.960779    0.069468   -0.018300   0.000000       0     106
C2   F15   2.979400    0.101646   -0.016400   0.000000       0     106
C10   F20  2.979801    0.111970   -0.023600   0.000000       0     106
C11   F18  2.981194    0.112572   -0.023200   0.000000       0     106
C9   F22   2.989427    0.110868   -0.023300   0.000000       0     106
H7   F20   2.990032    0.295714    0.005800   0.000000       0     106
O6   C11   3.014179    0.107861   -0.013900   0.000000       0     106
C1   C12   3.014431    0.069067   -0.016200   0.000000       0     106
C2   F13   3.015068    0.095932   -0.016400   0.000000       0     106
F14   F16  3.017495    0.187754   -0.014600   0.000000       0     106
C12   F16  3.036217    0.113775   -0.018900   0.000000       0     106
F5   F14   3.047688    0.108262   -0.016800   0.000000       0     106
C9   C10   3.054023    0.069468   -0.017700   0.000000       0     106
C1   F20   3.066717    0.103049   -0.017600   0.000000       0     106
F3   C8    3.071125    0.136530   -0.018500   0.000000       0     106
C9   F14   3.076169    0.115579   -0.018400   0.000000       0     106
C1   F18   3.077846    0.103049   -0.016300   0.000000       0     106
C8   F16   3.133166    0.117584   -0.012100   0.000000       0     106
F5   H7    3.181713    0.256119   -0.031900   0.000000       0     106
H7   C8    3.191555    0.096333   -0.007500   0.000000       0     106
H7   C11   3.353732    0.245823   -0.008800   0.000000       0     107
F4   F16   3.363307    0.115226   -0.004300   0.000000       0     107
F3   F15   3.431130    0.243781    0.007900   0.000000       0     107
F16   F20  3.483088    0.072016   -0.011400   0.000000       0     107
H7   F13   3.491804    0.158221    0.005600   0.000000       0     107
O6   F14   3.495897    0.072124   -0.015200   0.000000       0     107
H7   F18   3.499233    0.220456    0.008200   0.000000       0     107
F20   F22  3.506105    0.071479   -0.011300   0.000000       0     107
F18   F22  3.516783    0.071586   -0.011100   0.000000       0     107
C1   F22   3.518100    0.127157   -0.024800   0.000000       0     107
F14   F18  3.522450    0.072231   -0.010900   0.000000       0     107
O6   C12   3.531747    0.126190   -0.009900   0.000000       0     107
C8   F20   3.550507    0.119203   -0.024000   0.000000       0     107
C11   F14  3.568245    0.127910   -0.019100   0.000000       0     107
F3   O6    3.601300    0.072661   -0.010500   0.000000       0     107
C9   F18   3.601433    0.119633   -0.021700   0.000000       0     107
O6   F16   3.619083    0.072984   -0.013300   0.000000       0     107
C12   F13  3.644358    0.072231   -0.017800   0.000000       0     107
F3   F13   3.684054    0.210890   -0.009800   0.000000       0     107
C10   F19  3.698800    0.072339   -0.018100   0.000000       0     107
C10   F16  3.705899    0.131779   -0.015700   0.000000       0     107
C8   F21   3.708030    0.072769   -0.016600   0.000000       0     107
F4   C8    3.712890    0.124685   -0.016100   0.000000       0     107
C11   F17  3.715073    0.072231   -0.018000   0.000000       0     107
F5   C9    3.720766    0.134896   -0.025800   0.000000       0     107
C1   F19   3.743008    0.073521   -0.017400   0.000000       0     107
C8   F15   3.747272    0.073199   -0.018200   0.000000       0     107
C9   F21   3.749411    0.072769   -0.016800   0.000000       0     107
C12   F15  3.755106    0.072769   -0.017800   0.000000       0     107
C9   F13   3.756369    0.073306   -0.016400   0.000000       0     107
C1   F17   3.769241    0.072984   -0.017600   0.000000       0     107
H7   C10   3.802905    0.161983    0.001000   0.000000       0     107
H7   F16   3.868388    0.176494   -0.028000   0.000000       0     107
F3   H7    3.873790    0.186813   -0.017900   0.000000       0     107
C2   C11   3.971900    0.069627   -0.022100   0.000000       0     108
C2   C10   4.003482    0.070128   -0.022600   0.000000       0     108
F5   F16   4.106520    0.225778   -0.008100   0.000000       0     109
F13   F22  4.116174    0.107607   -0.023500   0.000000       0     109
F4   F14   4.117088    0.211858    0.002100   0.000000       0     109
F4   F13   4.132199    0.131498   -0.028100   0.000000       0     109
O6   F17   4.140530    0.104448   -0.014300   0.000000       0     109
C11   F13  4.145834    0.075226   -0.019900   0.000000       0     109
C8   F19   4.154060    0.075917   -0.018000   0.000000       0     109
F14   F21  4.161864    0.110273   -0.021600   0.000000       0     109
F18   F19  4.184785    0.111556   -0.024900   0.000000       0     109
H7   C12   4.190704    0.196556   -0.001700   0.000000       0     109
F17   F20  4.202051    0.110865   -0.024600   0.000000       0     109
F16   F21  4.207769    0.111161   -0.022400   0.000000       0     109
F5   F15   4.218318    0.142654   -0.042600   0.000000       0     109
F5   C10   4.229794    0.079965   -0.022700   0.000000       0     109
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C10   F15  4.239352    0.076214   -0.019900   0.000000        0      109
F15   F22  4.245650    0.107508   -0.023800   0.000000        0      109
C9   F17   4.247085    0.077398   -0.018300   0.000000        0      109
C1   F21   4.257971    0.075720   -0.014200   0.000000        0      109
O6   F19   4.271484    0.104646   -0.018500   0.000000        0      109
H7   F14   4.302931    0.107481   -0.015700   0.000000        0      110
F14   F15  4.322643    0.117354   -0.020400   0.000000        0      110
F3   C11   4.325350    0.113690   -0.019700   0.000000        0      110
F13   F16  4.380943    0.118372   -0.013400   0.000000        0      110
F4   C11   4.396587    0.080306   -0.021000   0.000000        0      110
O6   F22   4.423391    0.113079   -0.019100   0.000000        0      110
C2   C12   4.437995    0.079695   -0.025000   0.000000        0      110
F13   F20  4.461388    0.153588   -0.025200   0.000000        0      110
F3   C10   4.466958    0.127532   -0.025000   0.000000        0      110
H7   F19   4.469800    0.249467   -0.020900   0.000000        0      110
F14   F19  4.490419    0.161527   -0.016800   0.000000        0      110
F14   F20  4.495637    0.113079   -0.024200   0.000000        0      110
F15   F18  4.503080    0.158270   -0.023600   0.000000        0      110
F3   F22   4.504831    0.227889   -0.042600   0.000000        0      110
C2   F20   4.510653    0.111451   -0.023700   0.000000        0      110
C2   F18   4.510725    0.109415   -0.023500   0.000000        0      110
O6   F21   4.522857    0.163665   -0.002700   0.000000        0      110
F16   F18  4.577196    0.114199   -0.020000   0.000000        0      110
F5   F18   4.620184    0.148092   -0.024200   0.000000        0      110
F16   F17  4.644910    0.169670   -0.013900   0.000000        0      110
C2   F22   4.645839    0.164784   -0.033400   0.000000        0      110
F13   F21  4.648483    0.086718   -0.017100   0.000000        0      110
F17   F19  4.657663    0.087736   -0.015700   0.000000        0      110
F3   C12   4.680406    0.129568   -0.029300   0.000000        0      110
F4   F20   4.729524    0.136489   -0.028300   0.000000        0      110
F13   F15  4.734922    0.086718   -0.018400   0.000000        0      110
F15   F21  4.742229    0.087939   -0.016300   0.000000        0      110
F5   C11   4.896733    0.111496   -0.031000   0.000000        0      111
C2   F19   4.936791    0.084321   -0.023200   0.000000        0      111
C2   F17   4.943140    0.086619   -0.024900   0.000000        0      111
F5   F17   4.954540    0.083522   -0.021200   0.000000        0      111
F4   C10   4.963499    0.108099   -0.022300   0.000000        0      111
F3   F19   5.051138    0.149061   -0.019600   0.000000        0      111
H7   F17   5.060181    0.138771    0.000300   0.000000        0      111
F5   C12   5.066849    0.096710   -0.028300   0.000000        0      111
H7   F22   5.089364    0.182930   -0.017200   0.000000        0      111
H7   F21   5.127377    0.249767    0.012400   0.000000        0      111
F3   F20   5.166971    0.125279   -0.015800   0.000000        0      112
F4   C12   5.221077    0.100849   -0.022100   0.000000        0      112
F3   F17   5.225729    0.173231   -0.028100   0.000000        0      112
F4   F19   5.227674    0.084495   -0.018400   0.000000        0      112
F4   F18   5.265048    0.139513   -0.026800   0.000000        0      112
F3   F18   5.270566    0.124371   -0.022200   0.000000        0      112
F5   F20   5.306571    0.150416   -0.032300   0.000000        0      112
F5   F22   5.322773    0.176754   -0.034800   0.000000        0      113
F13   F19  5.405820    0.073388   -0.019200   0.000000        0      113
F15   F17  5.503685    0.073689   -0.019500   0.000000        0      113
F4   F22   5.543039    0.179461   -0.025600   0.000000        0      113
C2   F21   5.733992    0.075520   -0.022400   0.000000        0      114
F5   F19   6.007721    0.137624   -0.034900   0.000000        0      115
F3   F21   6.010382    0.113516   -0.027100   0.000000        0      115
F4   F17   6.047957    0.133005   -0.023800   0.000000        0      115
F5   F21   6.315151    0.104973   -0.024100   0.000000        0      116
F4   F21   6.456077    0.102163   -0.020200   0.000000        0      116
---------------------------------------------------------------------------
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Table 9-5: *Z-Matrix used in the refinement of the gas-phase structure of perfluorocyclohexan-1,1-diol. Distances r are given in Å, angles a and dihedrals d are given in °. The numbers written in line with the parameter indicate the groups they were refined in.*

```
----------------------------------------------------------
  1 C
  2 O   1    rcf1
  3 O   1     rco  2    afco
  4 H   3     roh  1    acoh  2   dfcoh
  5 C   1    rcc1  2   afcc1  3   aocc1 -1
  6 C   1    rcc2  2   afcc2  3   aocc2  1
  7 C   5    rcc3  1   accc1  2  dfccc1
  8 C   6    rcc4  1   accc2  2  dfccc2
  9 C   7    rcc5  8    rcc6  6   fcccc -4
 10 F   5    rcf2  1   accf1  2  dfccf1
 11 F   5    rcf3  1   accf2  3  doccf1
 12 F   6    rcf4  1   accf3  2  dfccf2
 13 F   6    rcf5  1   accf4  3  doccf2
 14 F   7    rcf6  5   accf5 10  dfccf3
 15 F   7    rcf7  5   accf6 11  dfccf4
 16 F   8    rcf8  6   accf7 12  dfccf5
 17 F   8    rcf9  6   accf8 13  dfccf6
 18 F   9   rcf10  7   accf9  8  accf11 -1
 19 F   9   rcf11  7  accf10  8  accf12  1
 20 H   2    roh2  1   acoh2  3   docoh

 Variables:
   rcf1        1.37821639         1
    rco        1.35751239         1
    roh        0.96681402        20
   rcc1        1.54699159         2
   rcc2        1.55296559         2
   rcc3        1.53976559         2
   rcc4        1.53817559         2
   rcc5        1.54172059         2
   rcc6        1.54022959         2
   rcf2        1.32637339         1
   rcf3        1.34804839         1
   rcf4        1.34291139         1
   rcf5        1.34242839         1
   rcf6        1.33321839         1
   rcf7        1.33171439         1
   rcf8        1.33274539         1
   rcf9        1.33415239         1
  rcf10        1.33013439         1
  rcf11        1.33487539         1
   roh2        0.96700902        20
   afco      111.17846643         3
   acoh      108.02410668         4
  afcc1      109.70161895         6
  aocc1      106.02661895         6
  afcc2      108.55561895         6
  aocc2      109.71461895         6
  accc1      115.13369311         5
  accc2      115.17269311         5
  accf1      109.38264010         7
  accf2      107.14864010         7
  accf3      107.56964010         7
  accf4      109.24964010         7
  accf5      108.68764010         7
  accf6      108.73164010         7
  accf7      108.88964010         7
  accf8      108.36864010         7
  accf9      108.72764010         7
 accf11      108.37064010         7
 accf10      108.56464010         7
 accf12      108.05764010         7
  acoh2      109.27510668         4
  dfcoh       65.21901580        10
 dfccc1     -170.58921345        12
 dfccc2      164.13698655        12
  fcccc     -133.30911068        21
 dfccf1       72.74386190        13
 doccf1     -163.91786886        14
 dfccf2      -71.57853810        13
 doccf2      170.05273114        14
 dfccf3      -65.52673810        13
 dfccf4      172.19403114        14
 dfccf5       70.36386190        13
 dfccf6     -163.27426886        14
  docoh      178.02639964        11
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***Table 9-6:** Cartesian coordinates for the refined structure of perfluorocyclohexan-1,1-diol.*

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-------------------------------------------------------------------------------------
 N | At | An |     Mass     |        X         |        Y         |          Z
---------------------------------------------------------------------------------------
  1  C     6   12.00000000   -0.101141759579    1.528656723853    0.215534207411
  2  O     8   15.99491462   -0.205251312690    2.738169765175   -0.436937867025
  3  O     8   15.99491462   -0.024145319314    1.701598986988    1.559782100267
  4  H     1    1.00782503   -0.861836077234    2.078486743095    1.861376467658
  5  C     6   12.00000000    1.211319217446    0.823101542246   -0.200183289857
  6  C     6   12.00000000   -1.348263350322    0.670863986967   -0.131714220430
  7  C     6   12.00000000    1.349344425873   -0.634655169373    0.276023043867
  8  C     6   12.00000000   -1.222278004215   -0.827665089273    0.191585075081
  9  C     6   12.00000000    0.130184192503   -1.421962622684   -0.244263094242
 10  F     9   18.99840320    2.241101960286    1.443226029768    0.360405221590
 11  F     9   18.99840320    1.328824265762    0.957469673709   -1.536361503038
 12  F     9   18.99840320   -2.401573759003    1.211928094445    0.501687549962
 13  F     9   18.99840320   -1.540240909318    0.686536151745   -1.460252126985
 14  F     9   18.99840320    2.463414579007   -1.150266407053   -0.244038498435
 15  F     9   18.99840320    1.390417141414   -0.647682403254    1.607040146176
 16  F     9   18.99840320   -2.221617230472   -1.482073932304   -0.399414449853
 17  F     9   18.99840320   -1.393379826066   -0.990310210200    1.504685725377
 18  F     9   18.99840320    0.204159959861   -2.671020016553    0.207002564801
 19  F     9   18.99840320    0.167670869311   -1.430458698566   -1.578584966746
 20  H     1    1.00782503   -0.226824918196    2.585105342319   -1.391512278239
---------------------------------------------------------------------------------------
 Rotational constants (MHz):     558.01200190      539.73361179      399.01541392
```

Table 9-7: *Full listing of structural parameters of perfluorocyclohexan-1,1-diol. r_a, r_g, r_e values are given in Å. Errors correspond to one time standard deviation. For atom numbering, see Table S9*

```
----------------------------------------------------------------------------
  No.  Type       i     j     k     l    a-Value  g-Value  e-Value      Error
----------------------------------------------------------------------------
    1 stretch     1     2     0     0    1.38452  1.38644  1.37822    0.00017
    2 stretch     1     3     0     0    1.36601  1.36782  1.35751    0.00017
    3 stretch     1     5     0     0    1.55829  1.56017  1.54699    0.00038
    4 stretch     1     6     0     0    1.56487  1.56682  1.55297    0.00038
    5 stretch     2    20     0     0    0.98111  0.98606  0.96701    0.00441
    6 stretch     3     4     0     0    0.98111  0.98607  0.96681    0.00441
    7 stretch     5     7     0     0    1.55027  1.55210  1.53977    0.00038
    8 stretch     5    10     0     0    1.33297  1.33474  1.32637    0.00017
    9 stretch     5    11     0     0    1.35515  1.35701  1.34805    0.00017
   10 stretch     6     8     0     0    1.54928  1.55111  1.53818    0.00038
   11 stretch     6    12     0     0    1.34781  1.34966  1.34291    0.00017
   12 stretch     6    13     0     0    1.34913  1.35099  1.34243    0.00017
   13 stretch     7     9     0     0    1.55182  1.55366  1.54172    0.00038
   14 stretch     7    14     0     0    1.33932  1.34110  1.33322    0.00017
   15 stretch     7    15     0     0    1.33821  1.33999  1.33171    0.00017
   16 stretch     8     9     0     0    1.55113  1.55297  1.54023    0.00038
   17 stretch     8    16     0     0    1.33895  1.34073  1.33275    0.00017
   18 stretch     8    17     0     0    1.34055  1.34234  1.33415    0.00017
   19 stretch     9    18     0     0    1.33663  1.33841  1.33013    0.00017
   20 stretch     9    19     0     0    1.34058  1.34237  1.33488    0.00017
   21 bend        2     1     3     0                     111.17847    0.34944
   22 bend        2     1     5     0                     109.70162    0.08244
   23 bend        2     1     6     0                     108.55562    0.08244
   24 bend        1     2    20     0                     109.27511    0.64272
   25 bend        3     1     5     0                     106.02662    0.08244
   26 bend        3     1     6     0                     109.71462    0.08244
   27 bend        1     3     4     0                     108.02411    0.64272
   28 bend        5     1     6     0                     111.67260    0.35319
   29 bend        1     5     7     0                     115.13369    0.25178
   30 bend        1     5    10     0                     109.38264    0.06313
   31 bend        1     5    11     0                     107.14864    0.06313
   32 bend        1     6     8     0                     115.17269    0.25178
   33 bend        1     6    12     0                     107.56964    0.06313
   34 bend        1     6    13     0                     109.24964    0.06313
   35 bend        7     5    10     0                     104.02373    0.34153
   36 bend        7     5    11     0                     113.14767    0.51556
   37 bend        5     7     9     0                     107.95160    0.30670
   38 bend        5     7    14     0                     108.68764    0.06313
   39 bend        5     7    15     0                     108.73164    0.06313
   40 bend       10     5    11     0                     107.73703    0.31929
   41 bend        8     6    12     0                     110.95445    0.30780
   42 bend        8     6    13     0                     103.36158    0.43274
   43 bend        6     8     9     0                     112.85177    0.32450
   44 bend        6     8    16     0                     108.88964    0.06313
   45 bend        6     8    17     0                     108.36864    0.06313
   46 bend       12     6    13     0                     110.48188    0.35000
   47 bend        9     7    14     0                     109.36939    0.63416
   48 bend        9     7    15     0                     110.89694    0.89135
   49 bend        7     9     8     0                     113.69317    0.30465
   50 bend        7     9    18     0                     108.72764    0.06313
   51 bend        7     9    19     0                     108.56464    0.06313
   52 bend       14     7    15     0                     111.11985    0.40475
   53 bend        9     8    16     0                     110.08891    0.65969
   54 bend        9     8    17     0                     110.12598    0.73609
   55 bend        8     9    18     0                     108.37064    0.06313
   56 bend        8     9    19     0                     108.05764    0.06313
   57 bend       16     8    17     0                     106.28547    0.34354
   58 bend       18     9    19     0                     109.36494    0.21206
   59 torsion    20     2     1     3                     178.02640    1.14626
   60 torsion     2     1     3     4                      65.21902    1.14269
   61 torsion    20     2     1     5                      61.07542    1.16447
   62 torsion     2     1     5     7                    -170.58921    0.34463
   63 torsion     2     1     5    10                      72.74386    0.39745
   64 torsion     2     1     5    11                     -43.77789    0.74594
   65 torsion    20     2     1     6                     -61.19901    1.16164
   66 torsion     2     1     6     8                     164.13699    0.34463
   67 torsion     2     1     6    12                     -71.57854    0.39745
   68 torsion     2     1     6    13                      48.37784    0.40131
   69 torsion     4     3     1     5                    -175.60770    1.15445
   70 torsion     3     1     5     7                      69.27080    0.42656
   71 torsion     3     1     5    10                     -47.39612    0.30227
   72 torsion     3     1     5    11                    -163.91787    0.46070
   73 torsion     4     3     1     6                     -54.87103    1.16342
   74 torsion     3     1     6     8                     -74.18812    0.59940
   75 torsion     3     1     6    12                      50.09636    0.72909
   76 torsion     3     1     6    13                     170.05273    0.46070
   77 torsion     7     5     1     6                     -50.18984    0.33872
   78 torsion    10     5     1     6                    -166.85677    0.29097
   79 torsion    11     5     1     6                      76.62149    0.57780
   80 torsion     5     1     6     8                      43.06906    0.45039
   81 torsion     5     1     6    12                     167.35354    0.55656
   82 torsion     5     1     6    13                     -72.69009    0.38594
```

```
 83 torsion    1    5    7    9                    56.27199   0.53080
 84 torsion    1    5    7   14                   174.80191   0.54678
 85 torsion    1    5    7   15                   -64.11076   0.92336
 86 torsion    1    6    8    9                   -44.58897   0.62943
 87 torsion    1    6    8   16                  -167.14678   0.60140
 88 torsion    1    6    8   17                    77.64457   0.61339
 89 torsion    9    7    5   10                   175.94335   0.45688
 90 torsion   14    7    5   10                   -65.52674   0.39745
 91 torsion   15    7    5   10                    55.56059   0.77670
 92 torsion    9    7    5   11                   -67.42321   0.65407
 93 torsion   14    7    5   11                    51.10670   0.27578
 94 torsion   15    7    5   11                   172.19403   0.46070
 95 torsion    5    7    9    8                   -56.53645   0.35660
 96 torsion    5    7    9   18                  -177.34589   0.32611
 97 torsion    5    7    9   19                    63.75955   0.42536
 98 torsion    9    8    6   12                  -167.07833   0.64104
 99 torsion   16    8    6   12                    70.36386   0.39745
100 torsion   17    8    6   12                   -44.84479   0.40824
101 torsion    9    8    6   13                    74.49219   0.44720
102 torsion   16    8    6   13                   -48.06562   0.63239
103 torsion   17    8    6   13                  -163.27427   0.46070
104 torsion    6    8    9    7                    52.14292   0.25245
105 torsion    6    8    9   18                   173.15244   0.24806
106 torsion    6    8    9   19                   -68.43862   0.31359
107 torsion    8    9    7   14                  -174.62990   0.24313
108 torsion   18    9    7   14                    64.56065   0.23374
109 torsion   19    9    7   14                   -54.33390   0.31121
110 torsion    8    9    7   15                    62.47837   0.40432
111 torsion   18    9    7   15                   -58.33108   0.44813
112 torsion   19    9    7   15                  -177.22563   0.40093
113 torsion    7    9    8   16                   174.02727   0.64489
114 torsion    7    9    8   17                   -69.09853   0.44936
115 torsion   18    9    8   16                   -64.96320   0.61431
116 torsion   19    9    8   16                    53.44573   0.69677
117 torsion   18    9    8   17                    51.91100   0.45844
118 torsion   19    9    8   17                   170.31994   0.47590
```

Table 9-8: *Full listing of interatomic distances, refined vibrational amplitudes l and corrections of perfluorocyclohexanol (fluorine axial), all is given in Å. The numbers at the Gu column indicate the groups the amplitudes were refined in.*

```
---------------------------------------------------------------------------
 At1  At2       r_a          l         corr         a          Gr      Gu
---------------------------------------------------------------------------
 O2   H20   0.981109    0.069700   -0.014100   0.000000        0       0
 O3   H4    0.981114    0.069700   -0.014300   0.000000        0       0
 C5   F10   1.332973    0.048468   -0.006600   0.000000        0     100
 C9   F18   1.336634    0.048680   -0.006500   0.000000        0     100
 C7   F15   1.338214    0.048785   -0.006500   0.000000        0     100
 C8   F16   1.338945    0.048891   -0.006200   0.000000        0     100
 C7   F14   1.339318    0.048891   -0.006100   0.000000        0     100
 C8   F17   1.340552    0.048997   -0.006400   0.000000        0     100
 C9   F19   1.340575    0.048997   -0.005700   0.000000        0     100
 C6   F12   1.347811    0.049949   -0.004900   0.000000        0     100
 C6   F13   1.349128    0.050055   -0.006700   0.000000        0     100
 C5   F11   1.355148    0.050267   -0.007100   0.000000        0     100
 C1   O3    1.366012    0.049738   -0.008500   0.000000        0     100
 C1   O2    1.384516    0.051643   -0.006300   0.000000        0     100
 C6   C8    1.549276    0.053294   -0.011100   0.000000        0     101
 C5   C7    1.550266    0.053393   -0.010500   0.000000        0     101
 C8   C9    1.551130    0.053393   -0.010900   0.000000        0     101
 C7   C9    1.551821    0.053492   -0.010100   0.000000        0     101
 C1   C5    1.558292    0.054088   -0.011300   0.000000        0     101
 C1   C6    1.564866    0.055278   -0.011900   0.000000        0     101
 C1   H4    1.912368    0.100500   -0.017700   0.000000        0       0
 C1   H20   1.944598    0.101700   -0.017300   0.000000        0       0
 F16   F17  2.140671    0.057197   -0.006800   0.000000        0     102
 F10   F11  2.166877    0.057489   -0.006800   0.000000        0     102
 F18   F19  2.180445    0.057197   -0.005900   0.000000        0     102
 F14   F15  2.204919    0.057100   -0.007100   0.000000        0     102
 F12   F13  2.212059    0.057877   -0.005900   0.000000        0     102
 F11   H20  2.240752    0.255785    0.015400   0.000000        0     102
 O2   O3    2.267427    0.059528   -0.010400   0.000000        0     102
 C8   F13   2.271388    0.066908   -0.008100   0.000000        0     102
 C7   F10   2.275829    0.065646   -0.013100   0.000000        0     102
 H4   F12   2.327555    0.227041   -0.098100   0.000000        0     102
 O3   C5    2.340445    0.067199   -0.017600   0.000000        0     102
 C8   F18   2.344263    0.066034   -0.013400   0.000000        0     102
 C8   F19   2.344883    0.067199   -0.014900   0.000000        0     102
 C1   F11   2.346023    0.065549   -0.013600   0.000000        0     102
 C6   F17   2.346439    0.066811   -0.014200   0.000000        0     102
 C5   F15   2.347551    0.067394   -0.010600   0.000000        0     102
 C7   F18   2.348805    0.066131   -0.011500   0.000000        0     102
 C5   F14   2.350087    0.066131   -0.012600   0.000000        0     102
 C7   F19   2.351838    0.067102   -0.013200   0.000000        0     102
 C6   F16   2.352007    0.065937   -0.013300   0.000000        0     102
 C1   F12   2.357598    0.065160   -0.017900   0.000000        0     102
 C1   F10   2.362174    0.065937   -0.013900   0.000000        0     102
 C9   F14   2.363296    0.066131   -0.014300   0.000000        0     102
 C9   F17   2.369720    0.067297   -0.010400   0.000000        0     102
 C9   F16   2.370880    0.066131   -0.013200   0.000000        0     102
 C1   F13   2.375487    0.066520   -0.011500   0.000000        0     102
 C9   F15   2.379403    0.067005   -0.009800   0.000000        0     102
 F13   H20  2.386022    0.241025   -0.076400   0.000000        0     102
 C8   F12   2.389809    0.065646   -0.013500   0.000000        0     102
 O2   C6    2.397488    0.066034   -0.015600   0.000000        0     102
 O3   C6    2.401317    0.067005   -0.018700   0.000000        0     102
 O2   C5    2.406086    0.066908   -0.012300   0.000000        0     102
 C7   F11   2.425972    0.067102   -0.013500   0.000000        0     102
 O2   H4    2.456824    0.188100    0.022800   0.000000        0     102
 C5   C9    2.509910    0.061835   -0.017700   0.000000        0     103
 F13   F16  2.520090    0.104426   -0.011600   0.000000        0     103
 C5   H20   2.551224    0.182038    0.016300   0.000000        0     103
 H4   C6    2.554056    0.167993   -0.066000   0.000000        0     103
 C5   C6    2.575020    0.062200   -0.010000   0.000000        0     103
 C6   C9    2.582239    0.062656   -0.017400   0.000000        0     103
 C7   C8    2.593437    0.066520   -0.013200   0.000000        0     102
 F10   F15  2.593894    0.105976   -0.015200   0.000000        0     103
 O3   F10   2.597261    0.103331   -0.021100   0.000000        0     103
 C6   H20   2.605681    0.179485   -0.054400   0.000000        0     103
 O2   F11   2.607705    0.098863   -0.012900   0.000000        0     103
 C1   C7    2.622281    0.062747   -0.017000   0.000000        0     103
 C1   C8    2.629454    0.063385   -0.019900   0.000000        0     103
 F12   F17  2.644010    0.104061   -0.022500   0.000000        0     103
 F17   F18  2.662135    0.106159   -0.004900   0.000000        0     103
 O2   F13   2.669830    0.098133   -0.016800   0.000000        0     103
 F16   F19  2.677121    0.105703   -0.012200   0.000000        0     103
 F11   F19  2.678210    0.157505   -0.022600   0.000000        0     103
 O3   F12   2.678825    0.099957   -0.030900   0.000000        0     103
 F10   F14  2.679161    0.100231   -0.006900   0.000000        0     103
 F14   F19  2.684599    0.105429   -0.014400   0.000000        0     103
 F13   F19  2.735215    0.198543   -0.012600   0.000000        0     104
 F15   F18  2.737621    0.104973   -0.006100   0.000000        0     103
 F11   F14  2.738684    0.105064   -0.018400   0.000000        0     103
```

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O3   F15   2.751089    0.157049   -0.008400   0.000000        0      103
F14   F18  2.775600    0.101143   -0.015100   0.000000        0      103
F16   F18  2.787205    0.100960   -0.018500   0.000000        0      103
F15   F17  2.815470    0.163889   -0.008800   0.000000        0      103
O2   F12   2.851078    0.098771   -0.016600   0.000000        0      103
F12   F16  2.853304    0.100413   -0.006900   0.000000        0      103
C5   F19   2.864174    0.122767   -0.023800   0.000000        0      104
F11   F13  2.869234    0.189384    0.013600   0.000000        0      104
O2   F10   2.891400    0.100595   -0.010900   0.000000        0      103
C9   F13   2.958270    0.125602   -0.006200   0.000000        0      104
C9   F11   2.976573    0.124621   -0.015500   0.000000        0      104
C5   C8    2.981832    0.080246   -0.015200   0.000000        0      104
C8   F15   2.986925    0.125384   -0.010000   0.000000        0      104
C1   F15   2.992166    0.124294   -0.009300   0.000000        0      104
C6   F19   2.992867    0.128001   -0.025200   0.000000        0      104
O3   C7    3.017366    0.121350   -0.018600   0.000000        0      104
C1   C9    3.020476    0.080464   -0.025300   0.000000        0      104
C5   F13   3.027040    0.120587    0.002400   0.000000        0      104
C6   C7    3.037219    0.080246   -0.012700   0.000000        0      104
C7   F17   3.040124    0.105794   -0.013800   0.000000        0      103
C6   F11   3.041570    0.124730   -0.004800   0.000000        0      104
O3   F17   3.042331    0.156776   -0.021700   0.000000        0      103
O3   H20   3.089861    0.105650   -0.002500   0.000000        0      104
C1   F17   3.129885    0.124403   -0.019100   0.000000        0      104
O3   C8    3.137931    0.120914   -0.022700   0.000000        0      104
F10   H20  3.177475    0.280751    0.057300   0.000000        0      104
H4   C5    3.191822    0.109248   -0.010000   0.000000        0      104
H4   F17   3.201350    0.361215   -0.066500   0.000000        0      104
F12   H20  3.232943    0.291872   -0.039300   0.000000        0      104
H4   H20   3.345888    0.230052    0.006900   0.000000        0      104
F13   F17  3.421534    0.072031   -0.012100   0.000000        0      105
H4   C8    3.441130    0.280751   -0.070100   0.000000        0      104
O3   F11   3.478421    0.071711   -0.018600   0.000000        0      105
H4   F10   3.489253    0.156654    0.015700   0.000000        0      105
F17   F19  3.495544    0.071391   -0.011700   0.000000        0      105
C1   F19   3.505549    0.129335   -0.034600   0.000000        0      105
C6   F15   3.509843    0.127308   -0.008100   0.000000        0      105
F15   F19  3.511965    0.071391   -0.011100   0.000000        0      105
F11   F15  3.543554    0.071604   -0.013500   0.000000        0      105
O3   F13   3.546886    0.071817   -0.018500   0.000000        0      105
H4   F15   3.560525    0.246079   -0.015200   0.000000        0      105
C8   F11   3.570587    0.130189   -0.009600   0.000000        0      105
C5   F17   3.619807    0.128375   -0.017100   0.000000        0      105
C7   F13   3.620360    0.125280    0.000400   0.000000        0      105
C9   F10   3.629434    0.074592   -0.019600   0.000000        0      105
O3   C9    3.635306    0.123359   -0.024900   0.000000        0      105
C5   F18   3.676906    0.074699   -0.017800   0.000000        0      105
C6   F18   3.718897    0.074699   -0.018500   0.000000        0      105
C5   F12   3.719019    0.074378   -0.018100   0.000000        0      105
C6   F10   3.719858    0.074912   -0.015500   0.000000        0      105
H4   F13   3.724330    0.175008   -0.059500   0.000000        0      105
C8   F14   3.742642    0.074912   -0.017300   0.000000        0      105
C7   F16   3.747269    0.074912   -0.015500   0.000000        0      105
C9   F12   3.748656    0.075125   -0.019900   0.000000        0      105
C1   F16   3.754907    0.076833   -0.021400   0.000000        0      105
C1   F14   3.756649    0.075872   -0.019700   0.000000        0      105
O2   C8    3.783326    0.075872   -0.022400   0.000000        0      105
O2   C7    3.800170    0.076299   -0.018500   0.000000        0      105
H4   C7    3.870770    0.177569   -0.028400   0.000000        0      105
C8   H20   3.950345    0.183865   -0.058800   0.000000        0      105
C7   H20   3.964912    0.187600   -0.011200   0.000000        0      105
F10   F19  4.061414    0.127288   -0.022000   0.000000        0      106
F19   H20  4.112730    0.273984   -0.073500   0.000000        0      106
F13   F18  4.146214    0.129770   -0.011500   0.000000        0      106
C5   F16   4.155677    0.091516   -0.015800   0.000000        0      106
C8   F10   4.165130    0.090726   -0.020200   0.000000        0      106
F11   F18  4.199028    0.127626   -0.019300   0.000000        0      106
H4   F11   4.204771    0.125257   -0.009500   0.000000        0      106
O2   C9    4.204979    0.091855   -0.026900   0.000000        0      106
C7   F12   4.207306    0.091403   -0.020400   0.000000        0      106
O3   F14   4.210538    0.125482   -0.018300   0.000000        0      106
F15   F16  4.228513    0.129093   -0.013200   0.000000        0      106
C1   F18   4.233168    0.091178   -0.022400   0.000000        0      106
C9   H20   4.234828    0.187885   -0.051500   0.000000        0      106
C6   F14   4.242375    0.090952   -0.016500   0.000000        0      106
F14   F17  4.253245    0.122399   -0.015500   0.000000        0      105
F12   F19  4.253711    0.130786   -0.021600   0.000000        0      106
H4   C9    4.260485    0.248933   -0.056800   0.000000        0      106
F11   F12  4.265434    0.127062   -0.007000   0.000000        0      106
F10   F13  4.265696    0.125708   -0.001200   0.000000        0      106
O2   F15   4.276439    0.127288   -0.011700   0.000000        0      106
O3   F16   4.360155    0.125031   -0.023900   0.000000        0      106
O2   F19   4.375290    0.182355   -0.037100   0.000000        0      106
F12   F15  4.383879    0.179873   -0.018200   0.000000        0      106
O2   F17   4.390822    0.126498   -0.022400   0.000000        0      106
F13   F15  4.447354    0.116070   -0.000200   0.000000        0      107
F11   F16  4.462395    0.186079   -0.007100   0.000000        0      106
O3   F19   4.471309    0.128529   -0.033300   0.000000        0      106
H4   F16   4.513353    0.305919   -0.081900   0.000000        0      106
F11   F17  4.536112    0.130334   -0.013700   0.000000        0      106
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F10   F17  4.544365    0.182017   -0.023200   0.000000        0      106
F13   F14  4.570913    0.160587   -0.001200   0.000000        0      107
O3   F18   4.600487    0.158555   -0.017700   0.000000        0      107
F10   F18  4.611939    0.087510   -0.018500   0.000000        0      107
F10   F12  4.677880    0.085884   -0.027300   0.000000        0      107
F15   H20  4.693463    0.169430    0.003100   0.000000        0      107
O2   F16   4.700849    0.089339   -0.023500   0.000000        0      107
F12   F18  4.706207    0.088425   -0.020700   0.000000        0      107
F16   H20  4.710292    0.224924   -0.072900   0.000000        0      107
F14   F16  4.719436    0.088730   -0.020100   0.000000        0      107
O2   F14   4.740655    0.090152   -0.020600   0.000000        0      107
F14   H20  4.748363    0.233258   -0.004200   0.000000        0      107
F17   H20  4.792232    0.173597   -0.045400   0.000000        0      107
H4   F19   5.084550    0.204190   -0.064000   0.000000        0      107
H4   F14   5.109869    0.154082   -0.019200   0.000000        0      107
H4   F18   5.193620    0.275234   -0.052500   0.000000        0      107
F10   F16  5.410758    0.203824   -0.020900   0.000000        0      108
F12   F14  5.481221    0.204090   -0.021900   0.000000        0      108
O2   F18   5.496848    0.110453   -0.034100   0.000000        0      109
F18   H20  5.558203    0.240933   -0.047500   0.000000        0      110
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