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The Perfluorinated Alcohols $(F_5C_6)(F_3C)_2COH$ and $(F_5C_6)(F_{10}C_5)COH$: Synthesis, Theoretical and Acidity Studies, Spectroscopy and Structures in the Solid State and the Gas Phase

Supplementary Material

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Experimental details

General

Bromopentafluorobenzene was purchased from ChemPur in 99 % purity and purified by distillation after stirring over P_2O_5. Hexafluoroacetone and perfluorocyclohexanone were purchased from P&M Invest. The gaseous hexafluoroacetone was used without further purification, whereas the ketone was stirred over P_2O_5, then condensed. Diethyl ether was dried in a Grubbs apparatus and degassed prior to use. Raman spectra were recorded using a Bruker Vertex 70 spectrometer with a RAM II FT-Raman module (excitation wavelength 1064 nm, 20 mW laser power). ZnSe-ATR (attenuated total reflection) IR spectra were recorded on a Nicolet Magna-IR 760 FT-IR spectrometer. NMR spectra were recorded in purified deuterated solvents on a Bruker Avance 400 MHz spectrometer. Melting points were determined with a Krüss KSPS 1000 digital melting point analyzer. Crystal structures were determined at 110 K on a Rigaku R-Axis SPIDER diffractometer using a sealed-tube Mo source. Gas-phase electron scattering was recorded at room temperature on reusable Fuji imaging plates with a Balzers KD-G 2 Gas-Eldigraph, equipped with a Staib Instruments electron source (50 kV/200 nA).[1] Calculations were carried out with the TURBOMOLE program package.[2] Calculated compounds were investigated with DFT-BP86,[3,4] as well as second-order Møller-Plesset (MP2[5,6]) perturbation calculations. SV(P) and TZVPP[7] basis sets were used and the RI approximation[5,6]) was applied. Vibrational frequencies were calculated analytically with the AOFORCE module[8] at the BP86/SV(P) level, and the results were used to determine the zero point vibrational energy (ZPE) and to verify that the geometry optimization resulted in a local minimum on the potential energy hypersurface with no imaginary frequencies.

*Synthesis of 1,1,1,3,3,3-hexafluoro-2-pentafluorophenyl-^{i}propanol (**1**)*

Mg filings (2.50 g, 93.1 mmol) were weighed into a 250 ml round bottom flask fitted with a dropping funnel and reflux condenser (cooled to 0 °C). Diethyl ether (150 ml) was added and the flask kept at 0 °C. C_6F_5Br (11.1 ml, 89.0 mmol) was added dropwise over 30 minutes. The mixture turned turbid, then dark brown. The reaction was then stirred for 16 h at RT. The condenser and flask were cooled to –60 °C and gaseous hexafluoroacetone (109.8 mmol) was condensed into the flask. The flask was allowed to reach RT and the mixture was stirred for a further 12 h. The solvent was then removed under reduced pressure and the residue hydrolyzed with excess aqueous HCl (32 %, 30 ml). After stirring for 2 hours, HCl and water were removed by condensation under reduced pressure. MgBrCl was removed by filtration and washed twice with diethyl ether (50 ml). The filtrate was separated from the solvent by

fractioned distillation. To remove residual diethyl ether, the distillate was again distilled from concentrated H_2SO_4 (b.p. 162 °C) to afford 19.3 g (65 %) of clear colorless **1**. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 4.13 ppm (s). ^{13}C[^{1}H] NMR (50 MHz, $CDCl_3$, RT): δ = 79.1 (m, $^2J_{C,F}$ = 33 Hz), 105.4 (m, $^2J_{C,F}$ = 11 Hz), 121.6 (q, $^1J_C{}^1J_{C,F}$ = 288 Hz), 138.3 (m, $^1J_{C,F}$ = 253 Hz, $^2J_{C,F}$ = 12.4 Hz, $^2J_{C,F}$ = 18.7 Hz), 142.6 (m, $^1J_{C,F}$ = 259 Hz, $^2J_{C,F}$ = 13 Hz, $^3J_{C,F}$ = 6 Hz), 146.3 (d, $^1J_{C,F}$ = 259 Hz) ppm. ^{19}F NMR (377 MHz, $CDCl_3$, RT): δ = –76.2 (m, $^5J_{F,F}$ = 15 Hz), –132.8 (b), –138.4 (b), –148.9 (m, $^3J_{F,F}$ = 23 Hz, $^4J_{F,F}$ = 7 Hz), –160.2 (b) ppm. IR (ZnSe ATR): υ = 422 (vw), 449 (vw), 477 (w), 540 (w), 552 (w), 646 (vw), 713 (mw), 733 (m), 744 (mw), 775 (vw), 804 (mw), 944 (m), 956 (m), 988 (m), 1008 (mw), 1110 (m), 1120 (m), 1140 (ms), 1152 (m), 1226 (s), 1275 (ms), 1368 (w), 1420 (w), 1498 (vs), 1533 (ms), 1617 (w), 1654 (mw), 3610 (mw) cm^{-1}.

*Synthesis of 2,2,3,3,4,4,5,5,6,6-decafluoro-1-pentafluorophenyl-cyclohexanol (**2**)*

Mg filings (3.00 g, 123 mmol) were weighed into a 500 ml round bottom flask fitted with a dropping funnel and reflux condenser (cooled to 15 °C). Diethyl ether (200 ml) was added and the flask kept at 0 °C. C_6F_5Br (15.0 ml, 120 mmol) was added dropwise over 30 minutes. The mixture turned turbid, then dark brown. The reaction was then stirred for 16 h at RT. Perfluorocyclohexanone (19.0 ml, 117 mmol), dissolved in diethyl ether (20 ml), was added dropwise over 30 minutes. The reaction mixture was refluxed for 4 h and cooled to RT. Aqueous HCl (32 %, 30 ml) was added and the mixture stirred for 2 h. HCl and water were removed by condensation under reduced pressure and the product was isolated by sublimation (10^{-2} mbar, 50 °C) to afford 53.6 g (85 %) of solid colorless **2** (m.p. = 52 °C). ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 4.20 (t, $J_{H,F}$ = 6.2 Hz) ppm. ^{13}C[^{1}H] NMR (101 MHz, toluene-D_8): δ = 78.9 (m, $^2J_{C,F}$ = 26 Hz), 108.1 (b), 109.0 (b), 112.0 (b), 138.1 (d, $^1J_{C,F}$ = 247 Hz), 142.2 (d, $^1J_{C,F}$ = 260), 146.4 (d, $^1J_{C,F}$ = 258 Hz). ^{19}F NMR (377 MHz, toluene-D_8): δ = –113.6 (m, $^2J_{F,F}$ = 283 Hz, $^5J_{F,F}$ = 53 Hz), –117.7 (m, $^2J_{F,F}$ = 274 Hz), –121.3 (m, $^2J_{F,F}$ = 284 Hz), –131.2 (m, $^2J_{F,F}$ = 283 Hz), –132.9 (m, $^5J_{F,F}$ = 53 Hz), –135.8 (m, $^2J_{F,F}$ = 274 Hz), –140.7 (m, $^2J_{F,F}$ = 284 Hz), –146.7 (m, $^3J_{F,F}$ = 22 Hz, $^4J_{F,F}$ = 7 Hz), –159.0 (m) ppm. IR (Diamond ATR): υ = 476 (w), 513 (w), 584 (vw), 605 (vw), 622 (vw), 630 (w), 685 (vw), 730 (m), 787 (w), 849 (w), 917 (w), 947 (s), 992 (ms), 1017 (ms), 1034 (mw), 1105 (m), 1116 (m), 1137 (vw), 1155 (w), 1176 (m), 1183 (m), 1213 (s), 1239 (m), 1256 (w), 1307 (m), 1322 (m), 1345 (vw), 1383 (vw), 1405 (w), 1486 (vs), 1536 (m), 1616 (vw), 1651 (m), 3623 (m) cm^{-1}. FT-Raman: υ = 154 (w), 200 (w), 280 (vw), 291 (vw), 315 (vw), 343 (mw), 376 (m), 412 (vw), 451 (mw), 480 (m), 514 (m), 586 (ms), 630 (vw), 686 (vs), 919 (mw), 1087 (vw), 1139 (w), 1236 (w), 1259 (w), 1299 (w), 1322 (w), 1405 (w), 1652 (mw) cm^{-1}. The crystal structure of **2** was

submitted to the Cambridge Structural Database, from where it can be retrieved free of charge under the reference number CCDC 800116.

Acidity measurements

The pK_a measurement procedure as well as the definitions of K_a, pK_a and K_{AHA} are the same as in ref [31].

Experimental and calculated IR and Raman spectra

Table 1. Experimental and calculated IR and Raman spectra of neat **1**.

exp. IR [cm^{-1}][a]	**exp. Raman [cm]$^{-1}$**	**calc. band [cm^{-1}][b,c]**
	217 (w)	210
	235 (mw)	
	264 (m)	255
	292 (vw)	293
	306 (vw)	315
	331 (mw)	330
	347 (w)	
	356 (w)	353
	379 (m)	375
422 (vw)	424 (w)	418 (w)
449 (vw)	449 (m)	443 (w)
477 (w)	480 (w)	480 (w)
	499 (vs)	488
540 (w), 552 (w)	541 (vw), 553 (w)	536 (vw)
	588 (vs)	570
	619 (w)	600
646 (vw)	647 (vw)	638 (vw)
713 (mw)	714 (vw)	708 (mw)
733 (m)	734 (vs)	716 (mw)
744 (mw)		333 (vw) + 418 (w)
775 (vw)	775 (vw)	763 (vw)
804 (mw)	806 (m)	795 (w)
944 (m)	946 (vw)	407 (w) + 536 (vw)
956 (m)	956 (vw)	929 (ms)
988 (m)	993 (w)	980 (m)
1008 (mw)	1014 (w)	1010 (mw)
1110 (m), 1120 (m)	1112 (vw), 1122 (vw)	1111 (mw)
1140 (ms), 1152 (m)	1147 (w)	1155 (mw)
1226 (s)	1238 (w)	1226 (s)
1275 (ms)	1278 (vw)	1254 (vs)
1313 (vw)	1317 (vw)	1312 (vw)
1368 (w)	1367 (vw)	1358 (m)
1420 (w)	1427 (w)	1410 (w)
1498 (vs)	1492 (vw)	1500 (vs)
1533 (ms)	1535 (vw)	1532 (ms)
1617 (w)		1621 (w)
1654 (mw)	1656 (mw)	1639 (mw)
3610 (mw)		3543 (m)

[a] ZnSe ATR, corrected; [b] BP86/SV(P), C_1 symmetry, unscaled; [c] Raman intensities cannot be reliably predicted with this method, where applicable only IR intensities are given.

Table 2. Experimental and calculated IR and Raman spectra of **2**.

exp. IR [cm^{-1}][a]	**exp. Raman [cm^{-1}]**	**calc. band [cm^{-1}][b,c]**
	154 (w)	147
	200 (w)	196
	280 (vw)	288
	291 (vw)	298
	315 (vw)	308
	343 (mw)	355
	376 (m)	372
	412 (vw)	400
	451 (mw)	459
476 (w)		469 (vw)
	480 (m)	471
513 (w)	514 (m)	499 (vw)
584 (vw)	586 (ms)	586 (vw)
605 (vw)		609 (vw)
622 (vw)		614 (vw)
630 (w)	630 (vw)	622 (vw)
685 (vw)	686 (vs)	667 (vw)
730 (m)		713 (w)
787 (w)		778 (vw)
849 (w)		825 (vw)
917 (w)	919 (mw)	912 (vw)
947 (s)		948 (m)
992 (ms)		1002 (m)
1017 (ms)		1008 (ms)
1034 (mw)		1028 (w)
1105 (m)	1087 (vw)	1094 (w)
1116 (m)		1106 (vw)
1137 (vw)		1116 (vw)
1155 (w)	1139 (w)	1131 (vw)
1176 (m)		1155 (w)
1183 (m)		1167 (w)
1213 (s)		1218 (m)
1239 (m)	1236 (w)	1226 (m)
1256 (w)	1259 (w)	1262 (vw)
1307 (m)	1299 (w)	1287 (mw)
1322 (m)	1322 (w)	1301 (w)
1345 (vw)		1333 (vw)
1383 (vw)		1370 (vw)
1405 (w)	1405 (w)	1371 (vw)
1486 (vs)		1488 (vs)
1536 (m)		1531 (m)
1616 (vw)		1620 (vw)
1651 (m)	1652 (mw)	1632 (mw)
3623 (m)		3542 (m)

[a] ZnSe ATR, corrected; [b] BP86/SV(P), C_s symmetry, unscaled; [c] Raman intensities cannot be reliably predicted with this method, where applicable only IR intensities are given.

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Table 3. IR and Raman bands of compounds **1** and **2**, including assignment. Modes are described in terms of the closest comparable normal mode where applicable and in general terms if the entire molecule is involved in the vibration.

1 exp. IR [cm^{-1}][a]	**1** exp. Raman [cm^{-1}][b]	**1** Assignment[c]	**2** exp. IR [cm^{-1}][a]	**2** exp. Raman [cm^{-1}][b]	**2** Assignment[c]
	217 (w)	C-C, F-C-F		154 (w)	arom. C_6 out-of-plane
	235 (mw)	C_6 out-of-plane		200 (w)	C-C, F-C-F
	264 (m), 292 (vw), 306	C-C, C-F		280 (vw)	C-C, C-F, F-C-F
	(vw)	C-C, C-O-H twist		291 (vw)	C-C, C-O-H bend
	331 (mw)	C-C, C-F		315 (vw)	C-C, C-O-H twist
	347 (w)	C-O-H twist		343 (mw)	C-F, C-O-H bend
422 (vw)	356 (w), 379 (m)	C-O-H twist		376 (m)	C-C, C-O-H twist
449 (vw)	424 (w)	C-C		412 (vw)	C-O-H twist
477 (w)	449 (m)	C_6 out-of-plane		451 (mw)	C-C, F-C-F
	480 (w)	C_6 out-of-plane	476 (w)		C-C
540 (w), 552 (w)	499 (vs)	F-C-F		480 (m)	arom. C_6 out-of-plane
	541 (vw), 553 (w)	C_6 stretch	513 (w)	514 (m)	aliph. C_6 wagging
	588 (vs)	C_6 out-of-plane	584 (vw)	586 (ms)	aliph. C_6 stretch
646 (vw)	619 (w)	C_6 out-of-plane	605 (vw)		C-C, F-C-F
	647 (vw)	C-C, F-C-F	622 (vw)		arom. C_6 out-of-plane
713 (mw), 733 (m)	714 (vw), 734 (vs)	C-C, F-C-F	630 (w)	630 (vw)	C-C
744 (mw)		C_6 twist	685 (vw)	686 (vs)	aliph. C_6 stretch
775 (vw)	775 (vw)	C_6 stretch	730 (m)		C-C
804 (mw)	806 (m)	C-C	787 (w)		arom. C_6 twist
944 (m)	946 (vw)	C-O-H bend	849 (w)		aliph. C_6 twist
956 (m), 988 (m)	956 (vw), 993 (w)	C-C	917 (w), 947 (s)	919 (mw)	C-C, C-O-H bend
1008 (mw)	1014 (w)	C-C, C-F	992 (ms)	992 (ms)	C-C, C-F
1110 (m), 1120 (m)	1112 (vw), 1122 (vw)	C-C, C-F	1017 (ms)	1017 (ms)	C-C, C-F
1140 (ms), 1152 (m)	1147 (w)	C-C, C-F	1034 (mw), 1105 (m)	1034 (mw), 1105 (m)	C-C, C-O-H bend
1226 (s)	1238 (w)	C-C-C	1116 (m)	1116 (m)	C-C, C-F
1275 (ms)	1278 (vw)	C-C-C, C-O-H	1137 (vw)	1137 (vw)	C-C
1313 (vw)	1317 (vw)	C_6 stretch	1155 (w), 1176 (m)	1155 (w), 1176 (m)	C-C, C-F
1368 (w)	1367 (vw)	C-O-H bend	1183 (m)	1183 (m)	aliph. C_6 wagging
1420 (w)	1427 (w)	C_6 stretch	1213 (s), 1239 (m)	1213 (s), 1239 (m)	aliph. C_6 stretch
1498 (vs)	1492 (vw)	C_6 twist	1256 (w), 1307 (m)	1256 (w), 1307 (m)	arom. C_6 stretch
1533 (ms)	1535 (vw)	C_6 stretch	1322 (m), 1345 (vw)	1322 (m), 1345 (vw)	C-C, C-O-H bend
1617 (w)		C_6 stretch	1383 (vw)	1383 (vw)	not calculated
1654 (mw)	1656 (mw)	C_6 stretch	1405 (w), 1486 (vs)	1405 (w), 1486 (vs)	arom. C_6 stretch
3610 (mw), 3633 (w)		O-H stretch	1536 (m), 1616 (vw)	1536 (m), 1616 (vw)	arom. C_6 stretch
			1651 (m)	1651 (m)	arom. C_6 stretch
			3604 (mw), 3623 (m)	3604 (mw), 3623 (m)	O-H stretch

[a] ATR (ZnSe crystal, corrected for penetration depth); [b] FT-Raman (flame-sealed capillary); [c] based on BP86/SV(P) frequency calculation.

Additional NMR spectra

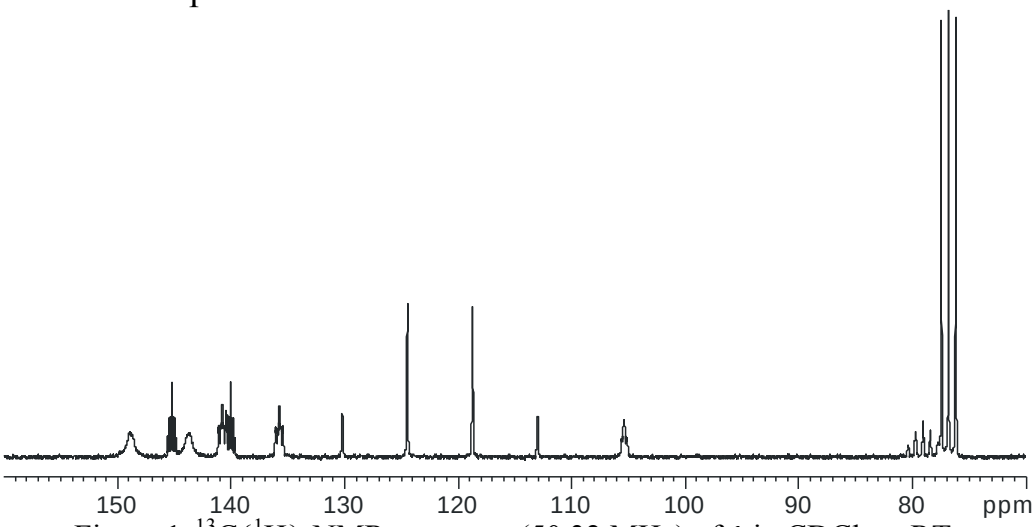

Figure 1. $^{13}C\{^{1}H\}$-NMR spectrum (50.32 MHz) of **1** in $CDCl_3$ at RT.

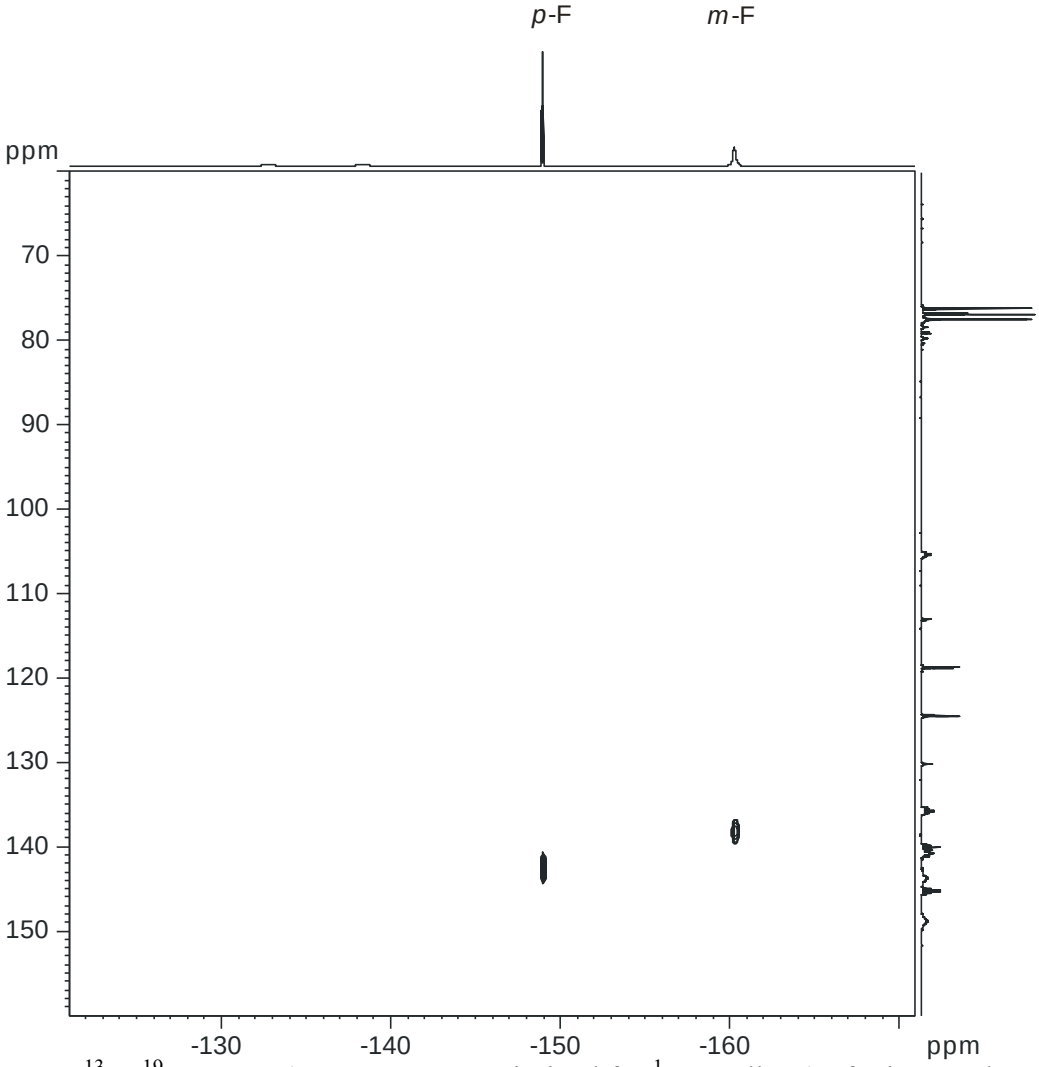

Figure 2. ^{13}C, ^{19}F HSQC (376.54 MHz, optimized for ^{1}J couplings) of **1** in $CDCl_3$ at RT (region of the resonances of the aromatic fluorine atoms).

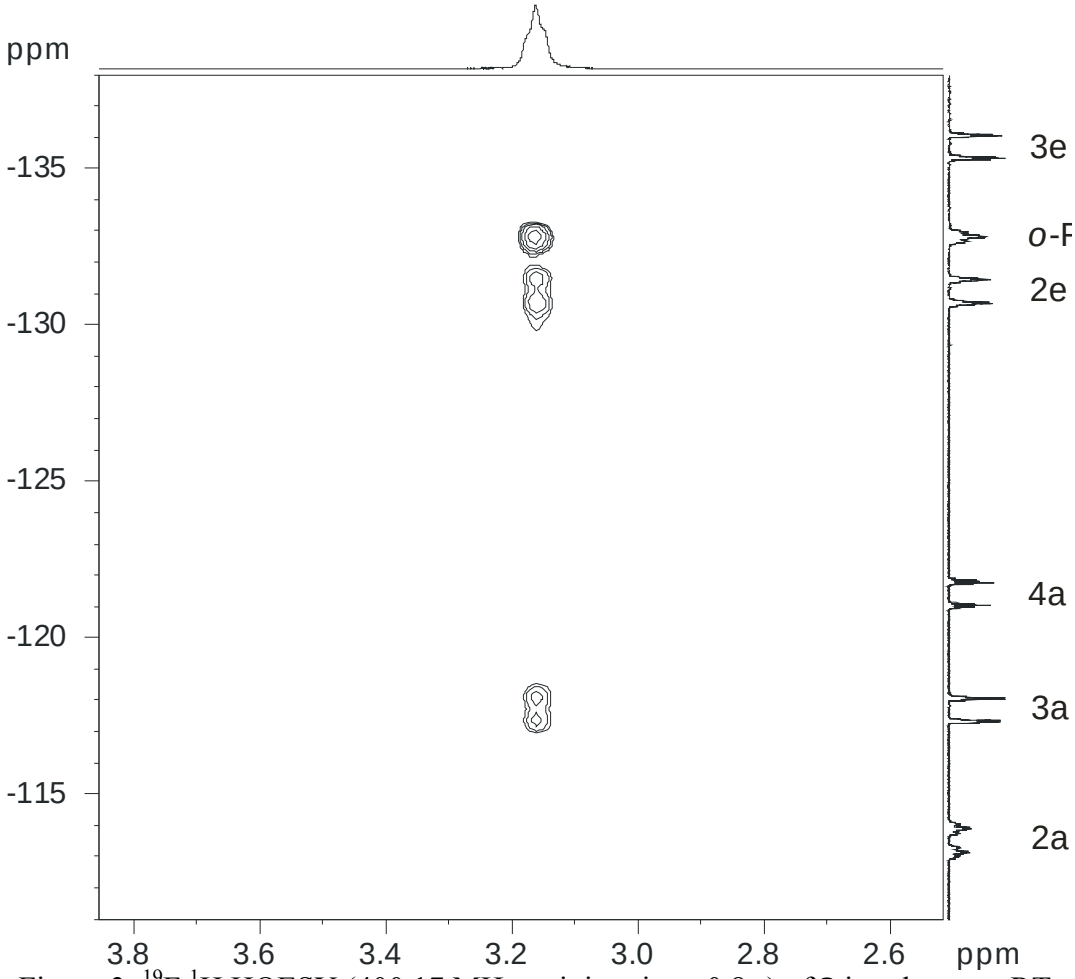

Figure 3. $^{19}F,^{1}H$ HOESY (400.17 MHz, mixing time: 0.8 s) of **2** in toluene at RT.

The $^{19}F,^{1}H$ HOESY shows NOEs (Fig. 3) between the signal of the proton of the OH-group and as well the *ortho*-fluorine atoms as the fluorine atoms 2e and 3a of the cyclohexyl ring. Especially the NOE to 3a proves that conformers with the proton pointing into the direction of the cyclohexyl group are also occupied in solution. However, according to the intensities of the NOEs the orientation of the proton to the perfluorophenyl group seems slightly favored.

Crystal structure analyses

2, and generally all crystals of compounds containing the $C_6F_5(C_6F_{10})$ ligand, dissolve slowly in perfluoroether oils. It is advisable to prepare samples in mineral oil or at low temperatures. The structure of **2** was submitted to the Cambridge Structural Database (Reference code CCDC 800116) and can be obtained free of charge.

Table 4. Crystal data and structure refinement parameters for compounds **2** and **2a**.

compound index number	**2**	**2a**
compound	**$C_6F_5(C_6F_{10})OH$**	**$C_6F_5(C_6F_{10})OH\cdot(^nC_4H_9)_4NBr\cdot H_2O$**
sum formula[a]	$C_{12}H_1O_1F_{15}$	$C_{28}H_{39}O_1Br_1F_{15}N_1$
T [K]	110(2)	110(2)
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	C2/c
a [Å]	12.051(3)	29.328(6)
b [Å]	15.155(3)	11.145(2)
c [Å]	15.655(3)	23.694(5)
α [°]	90	90
β [°]	110.91(3)	119.90(3)
γ [°]	90	90
V [Å^3]	2670.7(9)	6713.0(2)
Z	8	8
F(000)	1728	3200
ρ (calculated) [g cm^{-3}]	2.219	1.556
μ [mm^{-1}]	0.283	1.335
Crystal dimensions [mm]	0.18 x 0.08 x 0.08	0.2 x 0.1 x 0.1
θ range for data collection [°]	3.03 to 27.46	1.98 to 20.82
h,k,l index ranges	-13<=h<=15 -19<=k<=19 -20<=l<=20	-28<=h<=28 -11<=k<=11 -23<=l<=23
collected reflections	31176	5330
unique reflections	6035	2701
R_{int}	0.0642	0.0986
Completeness to θ_{max}	98.6 %	76.7 %
Absorption correction	empirical	empirical
Data / restraints / parameters	6035 / 0 / 514	2701 / 0 / 434
Goodness-of-fit on F^2 (S)	1.046	1.148
Final R_1 [I > 2σ(I)]	0.0476	0.0774
Final wR_2 [I > 2σ(I)]	0.1118	0.2074
Final R_1 (all data)	0.0665	0.0999
Final wR_2 (all data)	0.1218	0.2209
Largest peak and hole [e Å^{-3}]	0.430 and -0.305	0.385 and -0.382

[a] Of the monomer, where applicable.

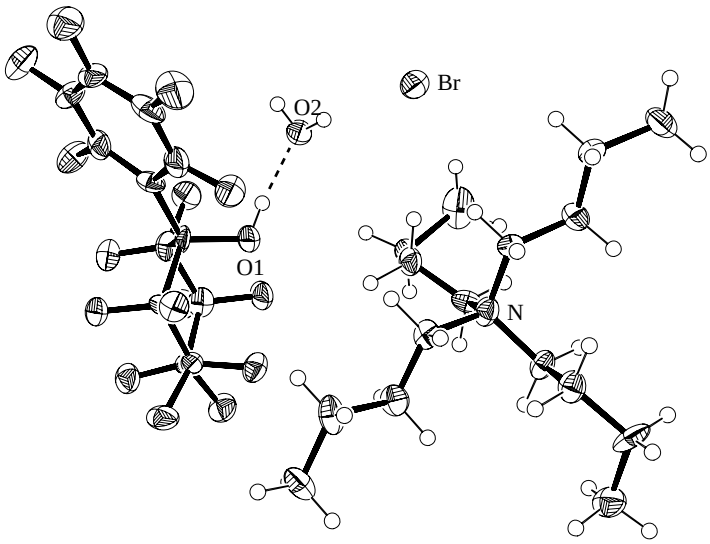

Figure 4. Asymmetric unit of the crystal structure of **2a**. Thermal ellipsoids are drawn at 50% probability level. Distances in pm: O1-O2 254.0(1), O1-C 139.1(1), H(bridge)-O2 171.1(1), N-C 151.4(1)-153.9(1). Angles in °: O1-H-O2 169.2(1), C-N-C 106.6(1)-111.4(1).

2a exhibits is a pronounced rotation of the C_6F_5 group with respect to the C_6F_{10} group with an angle of 51.6° between the two (cf. in **2**: 81.7 and 89.7°). This might be attributed to a rather short hydrogen bond with the water molecule (OH---O: 171.1(1) pm, O-O: 253.9(1) pm). Colorless platelets of **2a** were formed as side products in an attempt to synthesize the N^tBu_4 salt of a weakly coordinating anion containing the $C_6F_5(C_6F_{10})$ ligand. The crystal was twinned, but the resolution and data quality were too poor to resolve the twin law. Hydrogen atoms were not found on the Fourier map, but constrained to idealized positions. Thus, the structure is reported as preliminary and not deposited with the Cambridge Structural Database.

Table 5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **2a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
F(12)	-4742(3)	-4705(6)	-5710(3)	34(2)
F(5)	-3621(3)	-5460(6)	-6284(3)	40(2)
F(7)	-4200(3)	-8701(6)	-5503(3)	38(2)
F(15)	-4626(3)	-5087(6)	-6737(3)	33(2)
F(9)	-4465(3)	-6958(6)	-4904(3)	37(2)
F(14)	-5171(3)	-6576(6)	-7065(3)	34(2)
F(6)	-4971(3)	-8533(6)	-6365(3)	37(2)
F(1)	-4444(3)	-9310(6)	-6791(3)	42(2)
F(11)	-5668(3)	-6992(7)	-6327(3)	39(2)
F(10)	-5381(3)	-5908(7)	-5458(3)	40(2)
O(1)	-3990(3)	-6278(7)	-5561(4)	31(2)
F(2)	-3997(3)	-9768(7)	-7475(4)	51(2)
F(3)	-3378(3)	-8117(8)	-7619(3)	52(2)
F(4)	-3197(3)	-5976(8)	-7010(4)	54(2)
F(8)	-5059(3)	-8333(7)	-5357(3)	44(2)
F(13)	-5497(3)	-4878(7)	-6607(3)	42(2)
C(1)	-4080(4)	-7325(11)	-6513(5)	27(3)
C(12)	-4795(5)	-5997(11)	-6531(5)	29(3)
C(11)	-5061(5)	-5503(11)	-6168(5)	28(3)
C(10)	-5239(5)	-6461(12)	-5847(6)	32(3)
C(4)	-3605(5)	-7889(13)	-7266(6)	37(3)
C(3)	-3921(5)	-8709(11)	-7192(5)	33(3)
C(7)	-4337(5)	-6914(10)	-6117(5)	28(3)
C(2)	-4139(5)	-8424(11)	-6824(5)	34(3)
C(6)	-3742(5)	-6518(13)	-6578(6)	40(4)
C(9)	-4824(5)	-7394(12)	-5483(6)	36(3)
C(5)	-3510(5)	-6809(13)	-6944(6)	40(4)
C(8)	-4581(5)	-7929(11)	-5884(6)	33(3)
N(1)	-3112(4)	-2175(9)	-4214(4)	31(3)
C(1D)	-3152(5)	-1078(10)	-3845(5)	28(3)
C(2B)	-3295(5)	-4439(11)	-4254(5)	32(3)
C(3D)	-3076(6)	1120(11)	-3622(6)	41(4)
C(2D)	-3060(5)	112(11)	-4050(6)	35(3)
C(2C)	-4071(5)	-1917(12)	-5146(5)	35(3)
C(3A)	-1610(5)	-2357(11)	-3473(6)	33(3)
C(4D)	-3604(5)	1210(13)	-3635(6)	43(4)
C(2A)	-2099(5)	-2242(12)	-3447(6)	34(3)
C(1A)	-2569(5)	-2285(11)	-4133(5)	29(3)
C(1C)	-3497(5)	-2074(11)	-4938(5)	28(3)
C(1B)	-3235(5)	-3277(11)	-3928(6)	28(3)
C(4A)	-1109(5)	-2179(14)	-2807(6)	45(3)
C(3C)	-4393(5)	-1865(13)	-5897(6)	42(4)
C(4C)	-4980(5)	-1631(13)	-6139(6)	44(4)
C(3B)	-3339(5)	-5460(11)	-3844(5)	30(3)
C(4B)	-2808(7)	-5696(14)	-3205(7)	59(4)
Br(1)	-2115(1)	-5366(1)	-4460(1)	36(1)
O(2)	-3093(4)	-7246(11)	-4886(5)	33(2)

Table 6. List of bond lengths in the crystal structure of **2a**. H atoms were constrained to idealized geometries.

F(12)-C(11)	1.354(14)
F(5)-C(6)	1.324(16)
F(7)-C(8)	1.341(15)
F(15)-C(12)	1.326(15)
F(9)-C(9)	1.336(14)
F(14)-C(12)	1.358(14)
F(6)-C(8)	1.326(14)
F(1)-C(2)	1.360(15)
F(11)-C(10)	1.341(15)
F(10)-C(10)	1.337(14)
O(1)-C(7)	1.391(14)
F(2)-C(3)	1.319(15)
F(3)-C(4)	1.327(15)
F(4)-C(5)	1.370(16)
F(8)-C(9)	1.367(15)
F(13)-C(11)	1.369(14)
C(1)-C(2)	1.395(19)
C(1)-C(6)	1.40(2)
C(1)-C(7)	1.539(17)
C(12)-C(11)	1.522(17)
C(12)-C(7)	1.580(17)
C(11)-C(10)	1.545(19)
C(10)-C(9)	1.505(19)
C(4)-C(3)	1.37(2)
C(4)-C(5)	1.38(2)
C(3)-C(2)	1.351(18)
C(7)-C(8)	1.579(18)
C(6)-C(5)	1.38(2)
C(9)-C(8)	1.560(19)
N(1)-C(1A)	1.514(16)
N(1)-C(1C)	1.518(14)
N(1)-C(1B)	1.530(16)
N(1)-C(1D)	1.539(16)
C(1D)-C(2D)	1.484(18)
C(2B)-C(1B)	1.472(18)
C(2B)-C(3B)	1.542(18)
C(3D)-C(2D)	1.529(18)
C(3D)-C(4D)	1.54(2)
C(2C)-C(1C)	1.512(19)
C(2C)-C(3C)	1.544(17)
C(3A)-C(2A)	1.472(19)
C(3A)-C(4A)	1.542(17)
C(2A)-C(1A)	1.520(17)
C(3C)-C(4C)	1.54(2)
C(3B)-C(4B)	1.56(2)
O(2)-H(1)	0.79(14)
O(2)-H(2)	0.76(14)

Gas phase electron diffraction data

Table 7. GED data analysis parameters of **1**.

Dataset	**1**	**2**
R_g	6.43%	7.39%
R_d	4.26%	4.48%
Scale Factor, k	0.764(7)	0.750(11)
Correlation Parameter	0.4904	0.4896
Δs / nm^{-1}	2	2
s_{min} / nm^{-1}	24	56
s_{w1} / nm^{-1}	44	76
s_{w2} / nm^{-1}	136	276
s_{max} / nm^{-1}	158	320
Camera Distance / mm	503.5	252.78
Electron Wavelength / pm	5.36	5.37

Table 8. Refined atomic coordinates from GED (in Å).

	x	**y**	**z**
C1	2.020767	1.464336	0.000000
C2	2.188311	2.244124	1.166422
F3	1.938997	1.740896	2.379888
C4	2.318667	2.117524	-1.217079
F5	2.203637	1.493678	-2.414952
C6	2.903830	4.183048	-0.096109
C7	2.619737	3.575226	1.132292
F8	2.760056	4.264069	2.269702
C9	2.751505	3.447255	-1.277012
F10	3.018661	4.012915	-2.458770
F11	3.315521	5.450530	-0.140916
C12	1.548853	0.000000	0.000000
C13	2.045131	-0.858542	1.205260
F14	2.048225	-2.153628	0.886434
F15	3.302875	-0.521787	1.536674
F16	1.289167	-0.716234	2.300713
C17	0.000000	0.000000	0.000000
F18	-0.513389	-1.224636	0.145562
F19	-0.515218	0.770103	0.968875
F20	-0.438953	0.485527	-1.179660
O21	1.952537	-0.770852	-1.106031
H22	1.655232	-0.336182	-1.913542

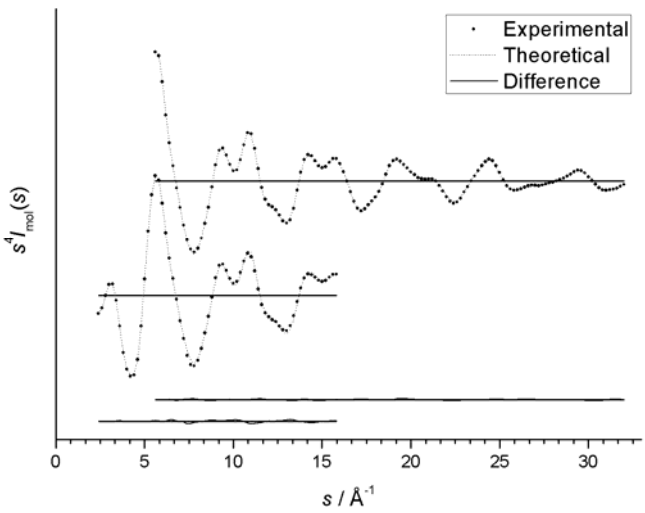

Figure 5. Experimental, theoretical and difference (experimental minus theoretical) molecular-scattering intensities.

Table 9. Inter-atomic distances (r_a), amplitudes of vibration (u_{h1}) and distance corrections for curvilinear perpendicular motion (k_{h1}).

	Amplitude	r_a [Å]	u_{h1} (GED)	k_{h1}	u_{h1} (B3LYP/6-31G**)
u22	O(21)-H(22)	0.962(10)	0.069(7)	0.003	0.068
u10	C(6)-F(11)	1.333(2)	0.042(2)	0.001	0.043
u16	C(13)-F(14)	1.333(2)	0.044(Tied to u_{10})	0.001	0.045
u19	C(17)-F(18)	1.335(2)	0.044(Tied to u_{10})	0.001	0.045
u11	C(7)-F(8)	1.337(2)	0.042(Tied to u_{10})	0.001	0.043
u12	C(9)-F(10)	1.337(2)	0.042(Tied to u_{10})	0.001	0.043
u4	C(2)-F(3)	1.337(2)	0.043(Tied to u_{10})	0.001	0.043
u18	C(13)-F(16)	1.338(2)	0.045(Tied to u_{10})	0.001	0.045
u20	C(17)-F(19)	1.340(2)	0.045(Tied to u_{10})	0.001	0.045
u17	C(13)-F(15)	1.343(2)	0.045(Tied to u_{10})	0.001	0.045
u21	C(17)-F(20)	1.349(3)	0.046(Tied to u_{10})	0.001	0.046
u6	C(4)-F(5)	1.355(2)	0.044(Tied to u_{10})	0.001	0.044
u7	C(4)-C(9)	1.399(2)	0.045(Tied to u_{10})	0.001	0.045
u8	C(6)-C(7)	1.399(2)	0.045(Tied to u_{10})	0.001	0.045
u5	C(2)-C(7)	1.399(2)	0.045(Tied to u_{10})	0.001	0.045
u9	C(6)-C(9)	1.400(2)	0.045(Tied to u_{10})	0.001	0.045
u15	C(12)-O(21)	1.407(5)	0.047(Tied to u_{10})	0.002	0.048
u1	C(1)-C(2)	1.412(3)	0.046(Tied to u_{10})	0.001	0.046
u2	C(1)-C(4)	1.413(3)	0.046(Tied to u_{10})	0.001	0.046
u3	C(1)-C(12)	1.538(6)	0.053(Tied to u_{10})	0.001	0.053
u14	C(12)-C(17)	1.549(5)	0.053(Tied to u_{10})	0.002	0.053
u13	C(12)-C(13)	1.560(6)	0.054(Tied to u_{10})	0.001	0.054
u193	C(12)-H(22)	1.938(15)	0.097(Tied to u_{110})	-0.003	0.098
u110	F(5)-H(22)	2.04(16)	0.193(20)	0.087	0.194
u201	F(14)-F(16)	2.153(3)	0.054(2)	0.000	0.058
u223	F(18)-F(19)	2.156(3)	0.055(Tied to u_{201})	0.000	0.059
u200	F(14)-F(15)	2.157(3)	0.054(Tied to u_{201})	0.000	0.059
u208	F(15)-F(16)	2.161(3)	0.055(Tied to u_{201})	0.000	0.060
u224	F(18)-F(20)	2.163(3)	0.055(Tied to u_{201})	0.000	0.059
u227	F(19)-F(20)	2.167(3)	0.055(Tied to u_{201})	0.000	0.059
u198	C(13)-O(21)	2.313(10)	0.071(Tied to u_{62})	0.000	0.067
u62	F(3)-C(7)	2.316(3)	0.063(2)	-0.003	0.060
u97	F(5)-C(9)	2.322(4)	0.063(Tied to u_{62})	-0.003	0.059
u192	C(12)-F(20)	2.359(9)	0.073(Tied to u_{62})	-0.001	0.068
u152	C(9)-F(11)	2.365(3)	0.065(Tied to u_{62})	-0.004	0.061
u112	C(6)-F(10)	2.366(2)	0.065(Tied to u_{62})	-0.004	0.061
u111	C(6)-F(8)	2.366(2)	0.065(Tied to u_{62})	-0.004	0.061
u126	C(7)-F(11)	2.368(3)	0.065(Tied to u_{62})	-0.001	0.061
u44	C(2)-F(8)	2.368(2)	0.065(Tied to u_{62})	-0.002	0.061
u81	C(4)-F(10)	2.368(2)	0.065(Tied to u_{62})	-0.002	0.061
u231	F(20)-H(22)	2.368(129)	0.245(fixed)	0.027	0.245
u221	C(17)-O(21)	2.371(10)	0.072(fixed)	0.000	0.072
u187	C(12)-F(14)	2.379(6)	0.071(Tied to u_{62})	-0.001	0.067
u41	C(2)-C(4)	2.386(5)	0.060(Tied to u_{62})	-0.003	0.056
u188	C(12)-F(15)	2.387(6)	0.074(Tied to u_{62})	-0.001	0.070
u23	C(1)-F(3)	2.394(3)	0.065(Tied to u_{62})	-0.001	0.061
u190	C(12)-F(18)	2.400(7)	0.074(Tied to u_{62})	0.000	0.070
u191	C(12)-F(19)	2.404(7)	0.075(Tied to u_{62})	-0.001	0.070
u124	C(7)-C(9)	2.412(5)	0.058(Tied to u_{62})	-0.003	0.055
u43	C(2)-C(6)	2.417(4)	0.059(Tied to u_{62})	-0.003	0.055
u78	C(4)-C(6)	2.417(4)	0.059(Tied to u_{62})	-0.003	0.055

u24	C(1)-F(5)	2.419(4)	0.063(Tied to u_{62})	-0.001	0.059
u189	C(12)-F(16)	2.421(6)	0.074(Tied to u_{62})	-0.001	0.070
u206	F(14)-O(21)	2.431(13)	0.110(Tied to u_{62})	0.008	0.104
u28	C(1)-C(9)	2.465(5)	0.059(Tied to u_{62})	-0.003	0.055
u26	C(1)-C(7)	2.465(5)	0.059(Tied to u_{62})	-0.003	0.055
u35	C(1)-C(17)	2.493(11)	0.078(Tied to u_{62})	-0.001	0.073
u39	C(1)-O(21)	2.493(11)	0.072(Tied to u_{62})	0.000	0.068
u194	C(13)-C(17)	2.521(14)	0.076(Tied to u_{62})	-0.001	0.072
u222	C(17)-H(22)	2.542(115)	0.179(fixed)	0.002	0.179
u83	C(4)-C(12)	2.555(5)	0.069(Tied to u_{62})	-0.004	0.065
u71	F(3)-F(16)	2.582(17)	0.150(Tied to u_{62})	0.048	0.142
u48	C(2)-C(12)	2.606(5)	0.073(Tied to u_{62})	-0.001	0.069
u31	C(1)-C(13)	2.614(9)	0.075(Tied to u_{62})	-0.001	0.071
u98	F(5)-F(10)	2.642(6)	0.113(Tied to u_{217})	-0.001	0.102
u109	F(5)-O(21)	2.643(23)	0.122(Tied to u_{217})	0.021	0.110
u63	F(3)-F(8)	2.649(5)	0.115(Tied to u_{217})	-0.002	0.104
u40	C(1)-H(22)	2.650(100)	0.175(Tied to u_{217})	0.009	0.158
u93	C(4)-H(22)	2.656(155)	0.212(Tied to u_{217})	0.038	0.192
u217	F(16)-F(19)	2.692(54)	0.189(7)	0.015	0.171
u230	F(20)-O(21)	2.699(29)	0.125(fixed)	0.002	0.125
u164	F(10)-F(11)	2.730(3)	0.120(Tied to u_{217})	-0.008	0.109
u215	F(16)-C(17)	2.731(20)	0.133(Tied to u_{217})	0.005	0.120
u140	F(8)-F(11)	2.736(3)	0.120(Tied to u_{217})	-0.003	0.108
u45	C(2)-C(9)	2.775(4)	0.069(Tied to u_{217})	-0.004	0.062
u79	C(4)-C(7)	2.775(4)	0.069(Tied to u_{217})	-0.004	0.063
u70	F(3)-F(15)	2.777(60)	0.230(Tied to u_{62})	0.023	0.216
u195	C(13)-F(18)	2.788(27)	0.140(Tied to u_{217})	0.002	0.126
u225	F(18)-O(21)	2.795(27)	0.151(Tied to u_{217})	0.001	0.136
u37	C(1)-F(19)	2.795(26)	0.142(Tied to u_{217})	0.000	0.129
u203	F(14)-F(18)	2.809(40)	0.247(Tied to u_{217})	0.007	0.223
u33	C(1)-F(15)	2.816(16)	0.145(Tied to u_{217})	0.004	0.131
u216	F(16)-F(18)	2.840(38)	0.240(Tied to u_{217})	0.005	0.217
u25	C(1)-C(6)	2.854(7)	0.068(Tied to u_{217})	-0.004	0.062
u68	F(3)-C(13)	2.875(23)	0.132(Tied to u_{217})	0.027	0.119
u38	C(1)-F(20)	2.891(28)	0.145(Tied to u_{217})	0.000	0.131
u100	F(5)-C(12)	2.909(7)	0.106(Tied to u_{217})	-0.002	0.096
u92	C(4)-O(21)	2.916(16)	0.100(Tied to u_{217})	0.006	0.091
u74	F(3)-F(19)	2.944(78)	0.432(Tied to u_{217})	0.014	0.391
u213	F(15)-O(21)	2.965(17)	0.164(Tied to u_{217})	-0.005	0.148
u67	F(3)-C(12)	2.973(6)	0.121(Tied to u_{217})	0.003	0.110
u51	C(2)-F(15)	3.008(34)	0.183(Tied to u_{217})	0.014	0.166
u196	C(13)-F(19)	3.037(33)	0.132(Tied to u_{217})	-0.001	0.120
u108	F(5)-F(20)	3.044(76)	0.382(Tied to u_{217})	0.005	0.346
u55	C(2)-F(19)	3.072(45)	0.254(Tied to u_{217})	0.007	0.230
u226	F(18)-H(22)	3.085(181)	0.262(Tied to u_{217})	-0.012	0.237
u202	F(14)-C(17)	3.088(22)	0.161(Tied to u_{217})	-0.005	0.145
u49	C(2)-C(13)	3.111(13)	0.098(Tied to u_{217})	0.008	0.088
u199	C(13)-H(22)	3.160(14)	0.097(fixed)	-0.024	0.097
u91	C(4)-F(20)	3.187(48)	0.237(Tied to u_{217})	0.000	0.215
u34	C(1)-F(16)	3.245(10)	0.123(Tied to u_{217})	-0.004	0.112
u52	C(2)-F(16)	3.301(14)	0.144(Tied to u_{217})	0.012	0.131
u53	C(2)-C(17)	3.330(26)	0.184(Tied to u_{228})	-0.005	0.154
u207	F(14)-H(22)	3.330(47)	0.129(fixed)	-0.026	0.129
u88	C(4)-C(17)	3.350(25)	0.161(Tied to u_{217})	-0.010	0.145
u219	F(16)-O(21)	3.461(9)	0.086(Tied to u_{228})	-0.008	0.073
u72	F(3)-C(17)	3.499(46)	0.320(Tied to u_{228})	-0.001	0.269

u105	F(5)-C(17)	3.559(43)	0.293(Tied to u_{228})	-0.011	0.246
u228	F(19)-O(21)	3.564(8)	0.081(3)	-0.008	0.068
u61	F(3)-C(6)	3.599(4)	0.073(Tied to u_{228})	-0.009	0.061
u94	F(5)-C(6)	3.609(4)	0.073(Tied to u_{228})	-0.009	0.061
u59	F(3)-C(4)	3.628(5)	0.073(Tied to u_{228})	-0.007	0.061
u125	C(7)-F(10)	3.629(4)	0.073(Tied to u_{228})	-0.010	0.061
u138	F(8)-C(9)	3.629(4)	0.073(Tied to u_{228})	-0.009	0.061
u82	C(4)-F(11)	3.631(4)	0.073(Tied to u_{228})	-0.010	0.061
u47	C(2)-F(11)	3.632(4)	0.073(Tied to u_{228})	-0.008	0.061
u42	C(2)-F(5)	3.651(5)	0.073(Tied to u_{228})	-0.007	0.061
u209	F(15)-C(17)	3.668(12)	0.088(Tied to u_{228})	-0.010	0.074
u27	C(1)-F(8)	3.670(4)	0.073(Tied to u_{228})	-0.008	0.062
u29	C(1)-F(10)	3.670(4)	0.074(Tied to u_{228})	-0.007	0.062
u197	C(13)-F(20)	3.686(13)	0.089(Tied to u_{228})	-0.008	0.075
u36	C(1)-F(18)	3.687(10)	0.085(Tied to u_{228})	-0.008	0.072
u32	C(1)-F(14)	3.714(9)	0.095(Tied to u_{228})	-0.008	0.079
u229	F(19)-H(22)	3.757(82)	0.202(Tied to u_{228})	-0.006	0.170
u57	C(2)-O(21)	3.769(11)	0.097(Tied to u_{228})	-0.011	0.082
u214	F(15)-H(22)	3.788(79)	0.203(Tied to u_{228})	-0.029	0.170
u90	C(4)-F(19)	3.789(44)	0.259(Tied to u_{228})	-0.018	0.217
u84	C(4)-C(13)	3.833(12)	0.100(Tied to u_{228})	-0.012	0.084
u153	C(9)-C(12)	3.856(6)	0.079(Tied to u_{228})	-0.010	0.066
u204	F(14)-F(19)	3.864(35)	0.217(Tied to u_{228})	-0.013	0.182
u127	C(7)-C(12)	3.890(6)	0.082(Tied to u_{228})	-0.008	0.069
u56	C(2)-F(20)	3.906(44)	0.252(Tied to u_{228})	-0.015	0.212
u86	C(4)-F(15)	3.923(25)	0.217(Tied to u_{228})	-0.004	0.182
u163	C(9)-H(22)	4.006(162)	0.203(fixed)	0.026	0.203
u58	C(2)-H(22)	4.036(94)	0.159(fixed)	-0.011	0.159
u211	F(15)-F(19)	4.057(33)	0.150(Tied to u_{64})	-0.008	0.139
u218	F(16)-F(20)	4.057(20)	0.123(Tied to u_{64})	-0.006	0.114
u64	F(3)-C(9)	4.105(4)	0.069(3)	-0.011	0.064
u210	F(15)-F(18)	4.105(25)	0.131(Tied to u_{64})	-0.013	0.122
u46	C(2)-F(10)	4.106(4)	0.069(Tied to u_{64})	-0.011	0.064
u80	C(4)-F(8)	4.107(4)	0.070(Tied to u_{64})	-0.011	0.065
u95	F(5)-C(7)	4.123(4)	0.070(Tied to u_{64})	-0.010	0.065
u205	F(14)-F(20)	4.155(34)	0.165(Tied to u_{64})	-0.012	0.153
u130	C(7)-F(15)	4.170(31)	0.229(Tied to u_{64})	0.009	0.212
u30	C(1)-F(11)	4.182(7)	0.069(Tied to u_{64})	-0.011	0.064
u69	F(3)-F(14)	4.188(23)	0.132(Tied to u_{64})	0.020	0.122
u134	C(7)-F(19)	4.188(43)	0.267(Tied to u_{64})	-0.005	0.248
u220	F(16)-H(22)	4.217(39)	0.111(fixed)	-0.027	0.111
u76	F(3)-O(21)	4.279(13)	0.110(Tied to u_{64})	-0.015	0.102
u162	C(9)-O(21)	4.289(15)	0.110(Tied to u_{64})	-0.004	0.102
u101	F(5)-C(13)	4.303(17)	0.104(Tied to u_{64})	-0.015	0.097
u161	C(9)-F(20)	4.328(48)	0.261(Tied to u_{64})	-0.011	0.242
u107	F(5)-F(19)	4.350(58)	0.324(Tied to u_{64})	-0.027	0.300
u113	C(6)-C(12)	4.384(7)	0.075(Tied to u_{64})	-0.012	0.070
u50	C(2)-F(14)	4.405(13)	0.098(Tied to u_{64})	-0.001	0.091
u75	F(3)-F(20)	4.419(57)	0.318(Tied to u_{64})	-0.019	0.294
u73	F(3)-F(18)	4.428(51)	0.292(Tied to u_{66})	-0.003	0.271
u128	C(7)-C(13)	4.467(12)	0.110(Tied to u_{64})	-0.002	0.101
u54	C(2)-F(18)	4.496(28)	0.158(Tied to u_{66})	-0.012	0.147
u103	F(5)-F(15)	4.551(36)	0.196(Tied to u_{66})	-0.011	0.182
u132	C(7)-C(17)	4.554(21)	0.165(Tied to u_{66})	-0.015	0.153
u89	C(4)-F(18)	4.564(23)	0.143(Tied to u_{66})	-0.019	0.133
u158	C(9)-C(17)	4.567(20)	0.161(Tied to u_{66})	-0.019	0.150

u106	F(5)-F(18)	4.587(45)	0.259(Tied to u_{64})	-0.017	0.240
u87	C(4)-F(16)	4.612(9)	0.121(Tied to u_{66})	-0.018	0.113
u175	F(10)-H(22)	4.618(169)	0.217(fixed)	0.038	0.217
u131	C(7)-F(16)	4.638(15)	0.146(Tied to u_{66})	0.000	0.136
u66	F(3)-F(11)	4.676(4)	0.082(3)	-0.014	0.076
u99	F(5)-F(11)	4.680(5)	0.081(Tied to u_{66})	-0.016	0.075
u212	F(15)-F(20)	4.715(11)	0.090(Tied to u_{66})	-0.016	0.083
u139	F(8)-F(10)	4.724(4)	0.081(Tied to u_{66})	-0.017	0.075
u85	C(4)-F(14)	4.744(13)	0.118(Tied to u_{66})	-0.022	0.109
u160	C(9)-F(19)	4.746(46)	0.259(Tied to u_{66})	-0.024	0.241
u77	F(3)-H(22)	4.748(56)	0.151(fixed)	-0.026	0.151
u60	F(3)-F(5)	4.797(6)	0.077(Tied to u_{66})	-0.011	0.072
u144	F(8)-F(15)	4.870(40)	0.254(Tied to u_{66})	0.011	0.236
u156	C(9)-F(15)	4.879(36)	0.243(Tied to u_{66})	-0.006	0.226
u135	C(7)-F(20)	4.889(47)	0.250(Tied to u_{66})	-0.022	0.232
u102	F(5)-F(14)	4.895(22)	0.138(Tied to u_{66})	-0.023	0.128
u165	F(10)-C(12)	4.914(5)	0.089(Tied to u_{66})	-0.015	0.082
u136	C(7)-O(21)	4.915(12)	0.103(Tied to u_{66})	-0.017	0.096
u120	C(6)-F(19)	4.917(39)	0.253(Tied to u_{66})	-0.017	0.235
u148	F(8)-F(19)	4.936(53)	0.338(Tied to u_{66})	-0.004	0.315
u141	F(8)-C(12)	4.966(5)	0.090(Tied to u_{66})	-0.012	0.084
u116	C(6)-F(15)	4.983(34)	0.253(Tied to u_{66})	0.000	0.235
u154	C(9)-C(13)	5.001(12)	0.106(Tied to u_{66})	-0.017	0.098
u123	C(6)-H(22)	5.025(149)	0.200(fixed)	0.005	0.200
u137	C(7)-H(22)	5.034(122)	0.182(fixed)	-0.010	0.182
u118	C(6)-C(17)	5.068(12)	0.149(Tied to u_{66})	-0.020	0.139
u121	C(6)-F(20)	5.069(44)	0.250(Tied to u_{66})	-0.020	0.233
u173	F(10)-F(20)	5.070(58)	0.326(Tied to u_{66})	-0.012	0.303
u174	F(10)-O(21)	5.078(18)	0.135(Tied to u_{66})	-0.003	0.125
u122	C(6)-O(21)	5.128(13)	0.112(Tied to u_{66})	-0.014	0.105
u145	F(8)-F(16)	5.195(17)	0.175(Tied to u_{66})	0.008	0.162
u104	F(5)-F(16)	5.261(9)	0.133(Tied to u_{66})	-0.023	0.123
u114	C(6)-C(13)	5.262(11)	0.114(Tied to u_{66})	-0.013	0.106
u142	F(8)-C(13)	5.277(16)	0.135(Tied to u_{66})	0.000	0.125
u65	F(3)-F(10)	5.434(4)	0.075(5)	-0.018	0.066
u96	F(5)-F(8)	5.452(4)	0.076(Tied to u_{65})	-0.018	0.067
u146	F(8)-C(17)	5.535(30)	0.228(Tied to u_{66})	-0.019	0.201
u170	F(10)-C(17)	5.557(30)	0.226(Tied to u_{66})	-0.025	0.199
u157	C(9)-F(16)	5.655(11)	0.135(Tied to u_{66})	-0.023	0.119
u117	C(6)-F(16)	5.669(13)	0.147(Tied to u_{66})	-0.016	0.130
u176	F(11)-C(12)	5.710(7)	0.062(Tied to u_{172})	-0.021	0.072
u129	C(7)-F(14)	5.748(13)	0.097(Tied to u_{172})	-0.013	0.112
u133	C(7)-F(18)	5.788(23)	0.127(Tied to u_{172})	-0.026	0.146
u159	C(9)-F(18)	5.841(19)	0.120(Tied to u_{172})	-0.031	0.138
u172	F(10)-F(19)	5.848(56)	0.252(19)	-0.036	0.292
u149	F(8)-F(20)	5.989(55)	0.272(Tied to u_{150})	-0.032	0.274
u155	C(9)-F(14)	6.013(13)	0.126(Tied to u_{150})	-0.030	0.127
u168	F(10)-F(15)	6.026(32)	0.247(Tied to u_{150})	-0.015	0.249
u150	F(8)-O(21)	6.088(13)	0.107(6)	-0.026	0.107
u183	F(11)-F(19)	6.112(41)	0.262(Tied to u_{150})	-0.026	0.264
u166	F(10)-C(13)	6.145(14)	0.110(Tied to u_{150})	-0.026	0.110
u179	F(11)-F(15)	6.186(25)	0.260(Tied to u_{150})	-0.006	0.262
u186	F(11)-H(22)	6.266(156)	0.208(fixed)	-0.003	0.208
u184	F(11)-F(20)	6.270(46)	0.258(Tied to u_{150})	-0.030	0.259
u151	F(8)-H(22)	6.286(114)	0.181(fixed)	-0.024	0.181
u181	F(11)-C(17)	6.347(13)	0.156(Tied to u_{150})	-0.030	0.157

u119	C(6)-F(18)	6.365(11)	0.125(Tied to u_{150})	-0.034	0.126
u185	F(11)-O(21)	6.416(14)	0.114(Tied to u_{150})	-0.023	0.115
u115	C(6)-F(14)	6.440(11)	0.126(Tied to u_{150})	-0.026	0.127
u177	F(11)-C(13)	6.552(11)	0.116(Tied to u_{150})	-0.021	0.117
u143	F(8)-F(14)	6.589(18)	0.135(Tied to u_{150})	-0.012	0.136
u147	F(8)-F(18)	6.697(35)	0.225(Tied to u_{169})	-0.030	0.204
u171	F(10)-F(18)	6.787(31)	0.216(Tied to u_{169})	-0.039	0.195
u169	F(10)-F(16)	6.892(10)	0.135(8)	-0.034	0.122
u180	F(11)-F(16)	6.909(14)	0.152(Tied to u_{169})	-0.023	0.137
u167	F(10)-F(14)	7.039(17)	0.166(Tied to u_{169})	-0.040	0.150
u182	F(11)-F(18)	7.651(12)	0.175(11)	-0.046	0.145
u178	F(11)-F(14)	7.737(12)	0.172(Tied to u_{182})	-0.037	0.143

Quantum chemical calculations

Table 10. Computational details for compounds **1** and **2**.

compound/symmetry	1 / C_1	2 / C_1	2 / C_s
minimized SCF energy [h] BP/SV(P)	-1515.9351	-2029.2208	-2029.2161
coordinates [Å] BP/SV(P)	O -1.609 1.451 -1.179 C -1.283 0.403 -0.306 C -2.120 -0.808 -0.886 F -1.425 -1.430 -1.860 F -3.264 -0.360 -1.415 F -2.440 -1.712 0.061 C -1.784 0.770 1.137 F -3.120 0.862 1.192 F -1.269 1.983 1.469 F -1.371 -0.116 2.064 C 0.242 0.134 -0.230 C 1.167 1.187 -0.420 C 2.557 1.015 -0.321 C 3.076 -0.241 0.028 C 2.193 -1.307 0.253 C 0.805 -1.105 0.154 F 0.038 -2.164 0.421 F 2.667 -2.506 0.593 F 4.390 -0.418 0.135 F 3.377 2.046 -0.529 F 0.759 2.445 -0.713 H -1.051 2.229 -0.953	C 2.426 1.243 0.430 C 3.108 0.074 -0.346 C 2.440 -1.316 -0.107 C 0.881 -1.276 -0.311 C 0.174 -0.113 0.477 C 0.870 1.275 0.235 C -2.292 -0.195 1.244 C -1.352 -0.036 0.192 C -1.913 0.190 -1.093 C -3.302 0.205 -1.318 C -4.196 0.014 -0.255 C -3.683 -0.180 1.034 F -1.168 0.410 -2.177 F -3.770 0.409 -2.550 F -5.511 0.033 -0.464 F -4.513 -0.335 2.067 F -1.925 -0.335 2.531 F 0.619 1.790 -0.989 F 0.353 2.138 1.167 F 2.934 2.413 -0.027 F 2.725 1.136 1.747 F 4.410 0.010 0.011 F 3.028 0.358 -1.672 F 2.751 -1.751 1.133 F 2.952 -2.192 -1.007 F 0.365 -2.454 0.113 F 0.669 -1.176 -1.646 O 0.474 -0.464 1.806 H 0.118 0.226 2.408	C -2.430 0.159 1.298 C -3.109 -0.379 0.000 C -2.430 0.159 -1.298 C -0.874 -0.043 -1.306 C -0.170 0.508 0.000 C -0.874 -0.043 1.306 F -2.968 -0.459 2.367 F -2.707 1.498 1.391 F -4.411 -0.014 0.000 F -3.030 -1.732 0.000 F -2.707 1.498 -1.391 F -2.968 -0.459 -2.367 F -0.368 0.624 -2.372 F -0.668 -1.370 -1.500 F -0.668 -1.370 1.500 F -0.368 0.624 2.372 C 1.350 0.221 0.000 O -0.340 1.904 0.000 C 2.307 1.277 0.000 C 3.695 1.030 0.000 C 4.192 -0.278 0.000 C 3.281 -1.341 0.000 C 1.897 -1.092 0.000 F 1.139 -2.191 0.000 F 3.722 -2.601 0.000 F 5.504 -0.508 0.000 F 4.540 2.064 0.000 F 1.991 2.571 0.000 H -1.296 2.133 0.000
minimized SCF energy [h] BP/TZVPP	-1517.7323	-2031.6216	-2031.6174
coordinates [Å] BP/TZVPP	O -1.589 1.428 -1.205 C -1.275 0.396 -0.304 C -2.096 -0.829 -0.894 F -1.372 -1.457 -1.850 F -3.231 -0.393 -1.464 F -2.444 -1.730 0.047 C -1.824 0.779 1.121 F -3.165 0.870 1.133 F -1.324 1.998 1.465 F -1.444 -0.098 2.075 C 0.251 0.141 -0.189 C 1.173 1.182 -0.404 C 2.555 1.012 -0.317 C 3.078 -0.234 0.025 C 2.202 -1.286 0.279 C 0.822 -1.089 0.181 F 0.060 -2.153 0.467 F 2.682 -2.487 0.625 F 4.398 -0.410 0.118 F 3.375 2.047 -0.539 F 0.769 2.447 -0.691 H -1.038 2.203 -1.002	C 2.435 1.231 0.463 C 3.122 0.083 -0.344 C 2.444 -1.313 -0.141 C 0.882 -1.263 -0.346 C 0.166 -0.123 0.477 C 0.875 1.266 0.267 C -2.305 -0.213 1.230 C -1.363 -0.036 0.191 C -1.931 0.213 -1.080 C -3.312 0.230 -1.302 C -4.200 0.019 -0.252 C -3.686 -0.197 1.023 F -1.192 0.459 -2.169 F -3.783 0.458 -2.535 F -5.518 0.039 -0.460 F -4.518 -0.374 2.057 F -1.946 -0.380 2.521 F 0.628 1.809 -0.949 F 0.360 2.122 1.212 F 2.943 2.418 0.040 F 2.737 1.091 1.779 F 4.424 0.002 0.026 F 3.066 0.401 -1.666	C -2.435 0.158 1.300 C -3.116 -0.381 0.000 C -2.435 0.158 -1.300 C -0.875 -0.037 -1.307 C -0.164 0.512 0.000 C -0.875 -0.037 1.307 F -2.970 -0.470 2.370 F -2.725 1.495 1.407 F -4.421 -0.013 0.000 F -3.047 -1.737 0.000 F -2.725 1.495 -1.407 F -2.970 -0.470 -2.370 F -0.373 0.635 -2.377 F -0.662 -1.364 -1.513 F -0.662 -1.364 1.513 F -0.373 0.635 2.377 C 1.358 0.219 0.000 O -0.323 1.911 0.000 C 2.317 1.265 0.000 C 3.695 1.020 0.000 C 4.190 -0.279 0.000 C 3.283 -1.333 0.000 C 1.908 -1.084 0.000

		F 2.754 -1.783 1.089 F 2.957 -2.173 -1.061 F 0.367 -2.460 0.040 F 0.671 -1.132 -1.681 O 0.461 -0.522 1.794 H 0.102 0.129 2.419	F 1.154 -2.192 0.000 F 3.726 -2.598 0.000 F 5.505 -0.510 0.000 F 4.547 2.055 0.000 F 2.006 2.566 0.000 H -1.266 2.149 0.000
minimized SCF+MP2 energy [h] MP2/TZVPP	-1514.9934	-2027.9708	-2027.9656
coordinates [Å] MP2/TZVPP	O -1.583 1.384 -1.235 C -1.268 0.384 -0.311 C -2.078 -0.840 -0.850 F -1.364 -1.486 -1.776 F -3.203 -0.428 -1.417 F -2.412 -1.698 0.112 C -1.791 0.801 1.085 F -3.115 0.908 1.104 F -1.274 2.001 1.393 F -1.418 -0.057 2.035 C 0.238 0.134 -0.195 C 1.150 1.176 -0.400 C 2.524 1.009 -0.310 C 3.046 -0.231 0.024 C 2.177 -1.283 0.268 C 0.804 -1.092 0.171 F 0.047 -2.145 0.455 F 2.658 -2.473 0.605 F 4.356 -0.404 0.117 F 3.336 2.037 -0.526 F 0.741 2.427 -0.680 H -1.041 2.157 -1.050	C 2.378 1.182 0.581 C 3.072 0.146 -0.328 C 2.436 -1.260 -0.249 C 0.897 -1.219 -0.464 C 0.177 -0.190 0.452 C 0.841 1.207 0.378 C -2.264 -0.304 1.205 C -1.332 -0.086 0.174 C -1.896 0.249 -1.071 C -3.270 0.297 -1.280 C -4.152 0.036 -0.244 C -3.638 -0.258 1.007 F -1.166 0.555 -2.136 F -3.740 0.605 -2.482 F -5.459 0.086 -0.442 F -4.459 -0.479 2.026 F -1.902 -0.539 2.473 F 0.586 1.830 -0.781 F 0.305 1.952 1.377 F 2.862 2.399 0.287 F 2.671 0.913 1.862 F 4.364 0.061 0.018 F 2.989 0.582 -1.597 F 2.748 -1.822 0.923 F 2.967 -2.013 -1.229 F 0.397 -2.439 -0.206 F 0.703 -0.958 -1.765 O 0.474 -0.714 1.715 H 0.092 -0.147 2.393	C -2.406 0.161 1.283 C -3.071 -0.382 0.000 C -2.406 0.161 -1.283 C -0.867 -0.035 -1.287 C -0.177 0.511 0.000 C -0.867 -0.035 1.287 F -2.931 -0.462 2.342 F -2.694 1.479 1.382 F -4.365 -0.031 0.000 F -2.985 -1.721 0.000 F -2.694 1.479 -1.382 F -2.931 -0.462 -2.342 F -0.366 0.623 -2.346 F -0.655 -1.347 -1.472 F -0.655 -1.347 1.472 F -0.366 0.623 2.346 C 1.330 0.219 0.000 O -0.329 1.903 0.000 C 2.281 1.261 0.000 C 3.652 1.015 0.000 C 4.143 -0.277 0.000 C 3.242 -1.326 0.000 C 1.874 -1.082 0.000 F 1.127 -2.182 0.000 F 3.684 -2.578 0.000 F 5.448 -0.506 0.000 F 4.498 2.039 0.000 F 1.975 2.553 0.000 H -1.262 2.140 0.000

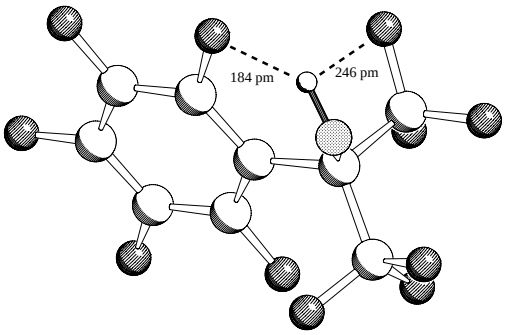

Figure 6. MP2/TZVPP (C_1) global minimum geometry of **1**.

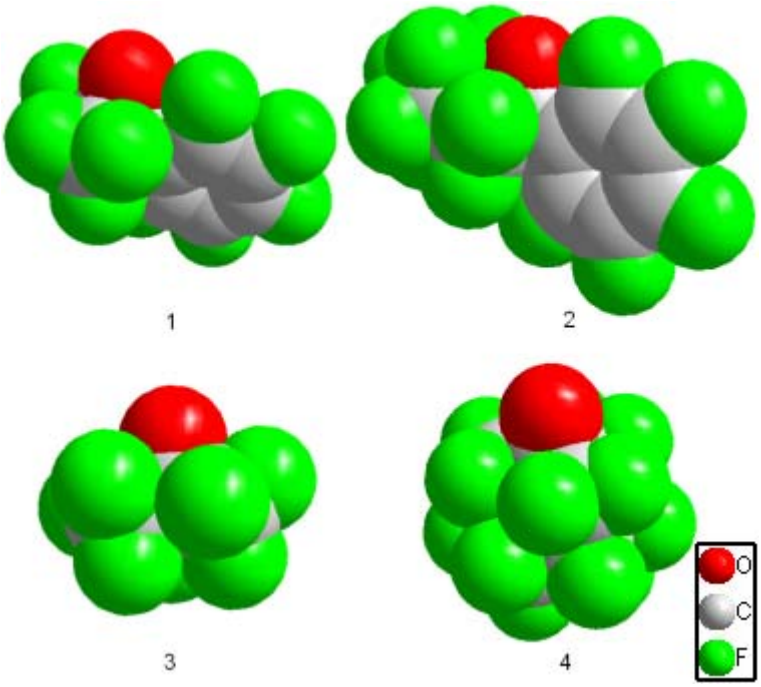

Figure 7. Calculated geometries of the anions of alcohols **1** to **4** (BP86/SV(P) level).

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