The $OC_2F_5^-$, $OCF(CF_3)_2^-$, and $OCFCF_2O^-$ Anions: Preparation and Structure

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The compounds $pip^+CF_3O^-$, $pip^+CF_3CF_2O^-$, $pip^+(CF_3)_2CFO^-$, and $(CH_3)_4N^+OCFCF_2O^-$ (pip^+ = 1,1,3,3,5,5-hexamethylpiperidinium) are obtained from pip^+F^- or $(CH_3)_4N^+F^-$ and COF_2, CF_3COF, $(CF_3)_2CO$, and $(COF)_2$. The structures of $pip^+CF_3CF_2O^-$, $pip^+(CF_3)_2CFO^-$, and $(CH_3)_4N^+OCFCF_2O^-$ have been investigated by single-crystal X-ray crystallography. Crystal data are as follows: for $pip^+CF_3CF_2O^-$, monoclinic $P2_1/c$, $a = 1300.7(1)$ pm, $b = 828.0(1)$ pm, $c = 1513.3(2)$ pm, $\beta = 110.13(1)°$, $Z = 4$; for $pip^+(CF_3)_2CFO^-$, monoclinic $P2_1/c$, $a = 1182.2(1)$ pm, $b = 1032.9(2)$ pm, $c = 1459.1(1)$ pm, $\beta = 107.45(1)°$, $Z = 4$; for $(CH_3)_4N^+OCFCF_2O^-$, tetragonal $P\bar{4}2_1/c$, $a = 1115.9(1)$ pm, $c = 1377.1(1)$ pm, $Z = 8$. All anion structures are indicative of a negative hyperconjugation effect. The structure of $FCOCF_2O^-$ is clearly nonsymmetric and resembles a close to planar cis oxygen configuration with one additional fluorine bound to one carbon atom. This fluorine atom is positioned slightly toward the second carbon atom, which corresponds to a movement from the asymmetric to the symmetric fluorine-bridged structure. Interionic forces seem to be responsible for this peculiar structure. These findings are compared with structures predicted by *ab initio* calculations.

Introduction

For some time the importance of negative hyperconjugation has been under discussion. First introduced in 1950 by Roberts to explain certain electronic influence of the CF_3 group,[1] it is now an established effect particularly in cases where fluorine is involved in bonding.[2,3]

One of the most prominent examples is the bond length and bond angle situation in CF_3O^-. $M^+CF_3O^-$ (compounds M = K^+, Rb^+, Cs^+) were first prepared in 1965.[4] Vibrational spectra analysis and force field calculations of CF_3O^- salts have already indicated a strong CO bond and rather weak CF bonds.[5−7] This finding has been further supported by *ab initio* calculations.[3,8] It also has been established that the F−C−O angles are much larger (and the F−C−F angles much smaller) than tetrahedral. But this entire structural behavior, which can conveniently be described by the valence bond formulation
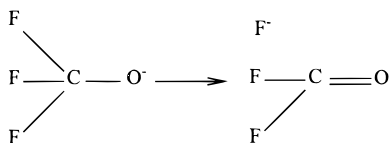
is supported only by one of the two known single-crystal structure determinations. In $[(CH_3)_2N]_3S^+CF_3O^-$ the anion is obviously well ordered, and bond lengths and angles agree fairly well with the predictions.[9]

In the single-crystal structure determination of the $Cs^+CF_3O^-$ salt, however, the anion appears disordered, and a disorder model at low temperatures resulted in a structure that is still

very close to regular tetrahedral.[10] Unfortunately the authors did not compare their results to the reported structure of $[(CH_3)N]_3S^+CF_3O^-$.[9] Even by making use of the 1,1,3,5,5,5-hexamethylpiperidinium cation, which is known in some cases to give well-ordered anions in otherwise problematic situations,[11,12] we could obtain only crystals that according to the single-crystal structure determination contained disordered anions. In the course of the discussion we will therefore only use data from the $[(CH_3)_2N]_3S^+CF_3O^-$ structure determination.[9] We have extended our investigation to compounds containing the anions $CF_3CF_2O^-$ and $(CF_3)_2CFO^-$ and can present here the first structure determinations of these anions. Also we present a crystal structure of the $COFCF_2O^-$ anion. This was particularly interesting because it could exist in several symmetric (fluoride bridged) or nonsymmetric conformations.

Experimental Section

General Procedures. All materials were handled in a drybox or in vacuum systems in order to avoid any hydrolysis. CF_3COF, $(CF_3)_2$-CO, and $(COF)_2$ were purchased from Fluorochem. Ltd., Old Glossop, Great Britain, and were used without further purification. Special care was taken to purify the solvents acetonitrile and propionitrile. Both were refluxed and distilled subsequently over $AlCl_3$, $KHSO_4$, $KMnO_4$, CaH_2, and P_2O_5 and stored over molecular sieves. 1,1,3,3,5,5-Hexamethylpiperidinium fluoride[11] and tetramethylammonium fluoride[13] were prepared according to literature procedures.

Physical Measurements. The IR spectra were recorded on a Perkin-Elmer 883 instrument; Raman spectra, on a Type 1403 of Spex Industries; and NMR spectra, on a FX 90Q multi nuclear instrument of JEOL, Ltd., Co., Tokyo, with 89.55 MHz for ^1H and 84.25 MHz for ^{19}F measurements. Chemical shifts are given for $CFCl_3$ and tetramethylsilane as standards. Dryboxes for the use of water-sensitive compounds were from Braun GmbH, Munich, Germany, and elemental analyses were performed by the Beller Co., Göttingen, Germany.

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.
(1) Roberts, J. D.; Webb, R. L.; McElhill, E. H. *J. Am. Chem. Soc.* **1950,** *72,* 408.
(2) Schleyer, P. v. R.; Kos, A. J. *Tetrahedron* **1983,** *39,* 1141.
(3) Reed, A. E.; Schleyer, P. v. R.; *J. Am. Chem. Soc.* **1990,** *112,* 1434.
(4) Redwood, M. E.; Willis, C. J. *Can. J. Chem.* **1965,** *43,* 1893.
(5) Redwood, M. E.; Willis, C. J. *Can. J. Chem.* **1967,** *45,* 389.
(6) Christe, K. O.; Curtis, E. C.; Schack, C. J. *Spectrochim. Acta* **1975,** *31A,* 1035.
(7) So, S. P. *Bull. Soc. Chim. Belg.* **1978,** *87,* 415.
(8) Francisco, J. S.; Williams, I. H. *Chem. Phys.* **1985,** *98,* 10.
(9) Farnham, W. B.; Smart, B. E.; Middleton, W. J.; Calabrese, J. C.; Dixon, D. A., *J. Am. Chem. Soc.* **1985,** *107,* 4565.

(10) Arlt, J.; Jansen, M. *Chem. Ber.* **1991,** *124,* 321.
(11) Mahjoub, A. R.; Zhang, X.; Seppelt, K. *Chem. Europ. J.* **1995,** *1,* 261.
(12) Zhang, X.; Seppelt, K. *Z. Anorg. Allg. Chem.* **1997,** *623,* 491.
(13) Christe, K. O.; Wilson, W. W.; Wilson, R. D.; Bau, R.; Feng, J. *J. Am. Chem. Soc.* **1990,** *112,* 7619.
(14) Program Gaussian 1994, Revision D4; Gaussian Inc.: Pittsburgh, PA, 1995.
(15) Becke, A. D. *J. Chem. Phys.* **1993,** *98,* 5648.
(16) Lee, C.; Young, W.; Parr, R. G. *Phys. Rev.* **1988,** *B37,* 785.

Table 1. Crystallographic Data

	pip⁺CF₃CF₂O⁻	pip⁺(CF₃)₂CFO⁻	(CH₃)₄N⁺OCFCF₂O⁻
formula	C₁₃H₂₄F₅NO	C₁₄H₂₄F₇NO	C₆H₁₂F₃NO₂
fw	305.33	355.34	187.17
λ (pm)	71.069	71.069	71.069
a (pm)	1300.7(1)	1182.2(1)	1115.9(1)
b (pm)	828.0(1)	1032.9(2)	1115.9(1)
c (pm)	1513.3(2)	1459.1(1)	1377.1(1)
β (deg)	110.13(1)	107.45(1)	
V (10^6 pm³)	1530.2(3)	1699.7(4)	1714.8(3)
temp (°C)	−143	−143	−143
space group	$P2_1/c$, No. 14	$P2_1/c$, No. 14	$P42_1/c$, No. 114
Z	4	4	8
μ (mm⁻¹)	0.12	0.14	0.15
ρ_{calcd}	1.325	1.389	1.450
R (wR_2)[a]	0.084 (0.2485)	0.051 (0.123)	0.027(0.069)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, w$R_2 = \{[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]\}^{1/2}$.

Table 2. Selected Bond Lengths (pm) and Angles (deg) in the Anions of [(CH₃)₂N]₃S⁺CF₃O⁻, pip⁺CF₃CF₂O⁻, and pip⁺(CF₃)₂CFO⁻

	X-ray	*ab initio*
[(CH₃)₂N]₃S⁺CF₃O⁻ [a]		
C−F	139.0	144.3
	139.0	144.3
	139.7	144.3
C−O	122.7	122.2
F−C−O	116.5	117.2
	116.5	117.2
	115.8	117.2
F−C−F	101.7	100.8
	101.7	100.8
	102.7	100.8
pip⁺CF₃CFO⁻		
C21−C22	152.1(5)	156.4
C21−F1	130.8(5)	136.1
C21−F2	131.5(5)	136.1
C21−F3	137.8(5)	136.1
C22−O1	123.0(4)	122.9
C22−F4	140.2(4)	147.6
C22−F5	144.7(4)	147.7
C22−C21−F1	115.5(3)	115.2
C22−C21−F2	113.0(3)	111.2
C22−C21−F3	109.1(3)	111.2
C21−C22−O1	117.8(3)	118.0
C21−C22−F4	105.3(3)	101.9
C21−C22−F5	99.3(3)	101.9
pip⁺(CF₃)₂CFO⁻		
CF₃	132.9(2)−133.8(2)	135.2−136.4
C23−O1	134.3(2)	125.6
C23−F1	141.6(2)	152.1
C21−C23−C22	113.71(1)	111.2
O1−C23−F1	114.97(1)	115.1
F1−C23−C21	104.51(1)	100.4
F1−C23−C22	105.57(1)	100.4
O1−C23−C21	108.91(1)	114.1
O1−C23−C22	109.22(1)	114.1

[a] X-ray data from ref 9. [b] Gaussian 6-3/+ρ(d,p) basis set, Becke 3LYP density functional.

X-ray Crystallographic Procedures. Single crystals were obtained as described in the experimental procedures. A suitable single crystal was cut, if necessary, and mounted on the Enraf-Nonius CAD 4 four-cycle diffractometer with help of a special device, which is a simplified construction of the one previously described.[17] Mo Kα radiation with a graphite monochromator was used. Lattice constants were obtained by fine adjustment of 25 reflections with θ values between 20 and 25°. X-ray intensities were measured with the ω-scan method, with maximal 60 s/reflection, allowing 25% of this time for background measurements. A Lorentz polarization correction was applied. The structures were solved and refined with the SHELX procedures.[18] No absorption or extinction corrections were applied. All atoms were refined anisotropically, and hydrogen atoms were refined isotropically with a single vibrational parameter for all hydrogen atoms. The identity of the oxygen atom was checked by exchange of this atom with one of the fluorine atoms bound to the same carbon atom. This exchange resulted in all cases in higher R-values, less uniform vibrational parameters, and less realistic bond lengths. Table 1 lists further crystallographic details. Table 2 lists important bond lengths and angles. Tables of atomic coordinates and anisotropic displacement parameters as well as complete tables of bond distances and angles and coordinates of hydrogen atoms are available as Supporting Information.

***Ab initio* Calculations**. The Gaussian 94 program set was used.[14] Predicted bond lengths are strongly dependent on basis sets used and the mode of electron correlation. We finally settled with the basis set 6-31+G(d,p) and the local density functional Becke 3[15] modified by Lee, Young, and Parr,[16] which gave reasonable results in an economical computation time.

1,1,3,3,5,5-Hexamethylpiperidinium Trifluoromethoxide, pip⁺-CF₃O⁻. A 100 mg (0.53 mmol) amount of pip⁺F⁻ was weighed into a polyperfluoroethylene−propylene (FEP) ampule equipped with a metal valve. On a glass vacuum line, 3 mL of acetonitrile was condensed into the tube, followed by 70 mg (1.0 mmol) of CF₂O. After the tube was closed and shaken while warming to room temperature and centrifuging the trace of insoluble residue was centrifuged into one end of the tube, it was slowly cooled to −40 °C, where colorless crystals appeared.

¹⁹F-NMR (CH₃CN, −40 °C): δ = −20 ppm, broad. Crystallographic data: a = 995.8(1), b = 1013.3(1), c = 1260.7(1) pm; V = 1360 × 10⁶ pm³; Z = 4, space group $P2_12_12_1$; d_c = 1.247 Mg m⁻³.

1,1,3,3,5,5-Hexamethylpiperidinium Pentafluoroethoxide, pip⁺-CF₂CF₂O⁻. A 100 mg (0.53 mmol) amount of pip⁺F⁻ was weighed into a FEP tube. On a metal vacuum line, 3 mL of acetonitrile and 125 mg (1.08 mmol) of CF₃COF were condensed into the tube. After the tube was closed and slowly warmed to room temperature under shaking and centrifuging the small insoluble residue was centrifuged to one end of the tube, it was gradually cooled to −40 °C. Within a few days colorless crystalline material appeared.

¹⁹F-NMR (CH₃CN, −40°C): δ = −82.5 (3F), −44.5 (2F, broad) ppm. IR (Nujol, only lines attributable to the anion are listed, cm⁻¹):

(17) Veith, M.; Bärnighausen, H. *Acta Crystallogr.* **1974**, *B30*, 1806.
(18) Sheldrick, G. SHELXS Program for Crystal Structure Solution, Göttingen 1986, and SHELXL-93, Göttingen, 1993.
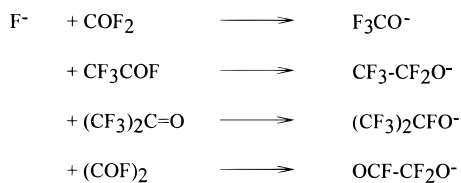
1599 (vs), 1280 (vs), 1173 (vs), 946 (vs), 823 (vs), 751 (s), 679 (s), 578 (m), 557 (m), 492 (m).

1,1,3,3,5,5-Hexamethylpiperidinium Heptafluoroisopropoxide, pip⁺(CF₃)₂CFO⁻. A 100 mg (0.53 mmol) amount of pip⁺F⁻ was weighed into a FEP tube. On a metal vacuum line 3 mL of propionitrile and 180 mg (1.08 mmol) of hexafluoroacetone were condensed into it. After slowly warming it to room temperature with shaking, the pip⁺F⁻ had completely dissolved while reacting. The excess of hexafluoroacetone was pumped off in a dynamic vacuum at room temperature. After the tube was closed, the solution was cooled slowly to −40 °C. Within a few days large crystals appeared. Anal. Calcd for C₁₄H₂₄-NF₇O: C, 47.32; H, 6.81; N, 3.94; F, 37.43. Found: C, 47.44; H, 6.88; N, 4.05; F, 37.10.

¹⁹F-NMR (C₂H₅CN, 25 °C): δ = −80.7 (6F), −68.6 (1F, broad) ppm. IR (Nujol, only bands attributable to the anion are listed, cm⁻¹): 1498, 1247, 1199, 1170, 955; 823, 742, 649, 550, 530, 510, 472, 425, 375. Raman (solid, cm⁻¹ only bands attributable to the anion): 1256 (20), 1144.5 (22), 942 (50), 745 (100), 650.5 (25), 551.5 (20), 512 (15, br), 480 (2), 426.5 (25), 377.5 (55).

Tetramethylammonium 1,2,2-Trifluoro-1-oxoethoxide, (CH₃)₄N⁺-COFCF₂O⁻. A 100 mg (1.07 mmol) of tetramethylammonium fluoride was weighed into a FEP tube. On a metal vacuum line, 4 mL of acetonitrile and 200 mg (2.13 mmol) of oxalyl fluoride were condensed into the tube. While warming to room temperature, the solid fluoride dissolved completely. In a dynamic vacuum, all volatile materials were pumped off at room temperature. A 190 mg amount (95% yield, based on (CH₃)₄N⁺F⁻) of a colorless, water-sensitive solid was obtained, mp 138−141 °C (dec). Anal. Calcd for C₆H₁₂NF₃O₂: C, 38.50; H, 6.46; N, 7.49; F, 30.45. Found: C, 37.40, H, 7.63; N, 7.60; F, 30.6.
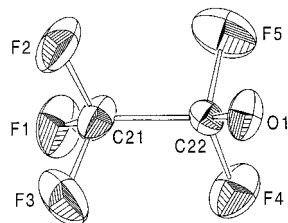
Figure 1. ORTEP diagram showing 50% probability ellipsoids for the anion $CF_3CF_2O^-$ with numbering scheme.

Recrystallization from acetonitrile at −40 °C gave needle-shaped single crystals suitable for the X-ray structure determination.

^{19}F NMR (CH₃CN): $\delta = -6.2$ (broad) ppm. IR (Nujol, only lines attributable to the anion are listed, cm⁻¹): 1843 (s), 1531 (s), 1170 (s), 949 (s), 827 (s), 748 (m), 706 (s), 653 (m), 526 (m), 479 (m). Raman (solid, cm⁻¹): 1844.9 (10), 1181.4 (4), 950.7 (80), 756.2 (100), 706.0 (5), 647.4 (6), 377.6 (20).

Results

The reactions of the fluorooxocarbon compounds with F⁻ occur spontaneously and quantitatively.

$$F^- \quad + COF_2 \longrightarrow F_3CO^-$$
$$+ CF_3COF \longrightarrow CF_3\text{-}CF_2O^-$$
$$+ (CF_3)_2C=O \longrightarrow (CF_3)_2CFO^-$$
$$+ (COF)_2 \longrightarrow OCF\text{-}CF_2O^-$$

Acetonitrile or propionitrile serve well both as reaction media and solvents for the recrystallization. The good solubility of 1,1,3,3,5,5-hexamethylpiperidinium fluoride, as compared to CsF, is also helpful in these reactions.

To our knowledge no experimental structures are known for $CF_3CF_2O^-$ and $(CF_3)_2CFO^-$. The formation of the $CF_3CF_2O^-$ anion had already been established by its ^{19}F NMR and IR spectra.[5] In the ^{19}F NMR spectra we observe two resonances with an intensity ratio of 3:2; without noticeable coupling the latter signal is broadened, maybe due to slow F⁻ exchange. The single-crystal structure determination reveals the ionic formulation pip⁺CF₃CF₂O⁻. The structure of the anion which is here of primary interest is shown in Figure 1. It is important to note that the oxygen and fluorine positions could be clearly distinguished. The C−O bond length of 122.8 pm agrees well with that in CF_3O^- (122.7 pm),[9] and the two CF bonds in the $-CF_2O^-$ group are even a little longer (140.2, 144.7 pm) than those in CF_3O^- (139.0, 139.7 pm).[9] Also, all angles in which the oxygen atom is involved are much larger than the tetrahedral angle. Angles and distances in the staggered CF₃ group are normal.

The pip⁺(CF₃)₂CFO⁻ salt is prepared likewise from pip⁺F⁻ and (CF₃)₂CO. Its NMR and vibrational spectra are in accord with previous published data.[5] The NMR spectrum indicates the presence of six equivalent and one distinct fluorine atoms. Coupling between the two is, however, not observed, except some broadening for the single fluorine atom resonance, for which a septet splitting is to be expected. As in $CF_3CF_2O^-$, the $^3J_{CF-CF}$ coupling is again very small.

Recrystallization from propionitrile gave single crystals suitable for an X-ray structure determination. Again it is worth noticing that in the single-crystal structure oxygen and fluorine atoms on the central carbon atom could clearly be distinguished (see Figure 2). The two trifluoromethyl groups appear normal. The central carbon atom bears one oxygen atom (134.3(2) pm) and one fluorine atom (141.6(2) pm) besides the two CF₃ groups. The angle O−C−F is enlarged, as expected. Steric interaction
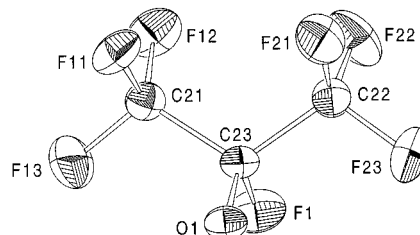

Figure 2. ORTEP diagram showing 50% probability ellipsoids for the anion $(CF_3)_2CFO^-$ with numbering scheme.
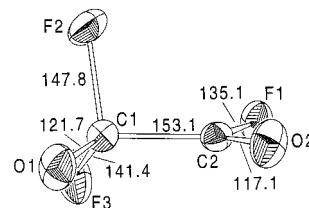

Figure 3. ORTEP diagram showing 50% probability ellipsoids for the anion $FCOCF_2O^-$ with numbering scheme,

between the two methylgroups also enlarges the C−C−C angle. Considering the longer C−O bond compared to that in $CF_3CF_2O^-$ and CF_3O^-, negative hyperconjugation seems to play a lesser role here than in the two previously mentioned systems; see the Discussion.

Oxalyl fluoride, COFCOF, a colorless gas, is known to be a Lewis acid. A crystalline 1:1 adduct with 1,4-dioxane[19] has been described. A reaction with F⁻ was first found by Ault in a matrix isolation study.[20] Infrared spectra were assigned in terms of two fluorine bridged anions having *cis* or *trans* structures with respect to the oxygen positions (Figure 3d,e), since it is known that gaseous oxalyl fluoride is a mixture of planar *cis* and *trans* molecules.[21] The first isolation of $[(CH_3)_2N]_3S^+C_2F_3O_2^-$ and $[(C_2H_5)_5N]_3S^+C_2F_3O_2^-$ and an analysis of their vibrational spectra indicated that the nonbridged form (Figure 3a−c) should prevail in the solid.[22] Ab initio calculations by the same group indicated that trifluoroacetate $CF_3CO_2^-$ is the overall minimum for this atomic combination but is unlikely to be formed in the COFCOF + F⁻ reaction. The three conformational isomers **a**−**c** of the open structure are lower in energy, whereas the symmetric, fluorine-bridged **d** and **e** structures are 32.6 and 34.2 kJ/mol (7.9 and 8.3 kcal/mol) higher in energy than conformer **a**.[22]
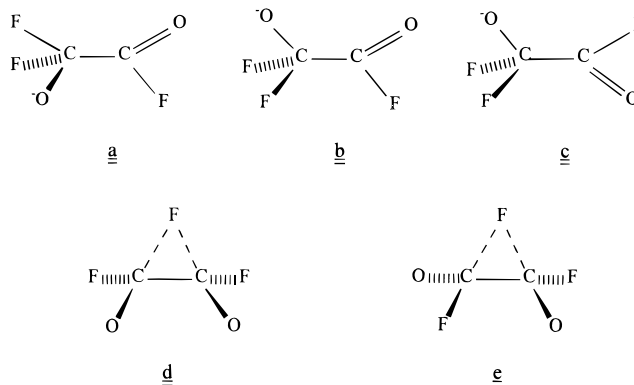
(19) Möller, G.; Olmstead, M. M.; Tinti, D. S. *J. Am. Chem. Soc.* **1987**, *109*, 95.
(20) Ault, B. S. *Inorg. Chem.* **1986**, *25*, 1013.
(21) Durig, J. R.; Brown, S. C.; Hannum, S. E. *J. Chem. Phys.* **1991**, *54*, 4428.
(22) Dixon, D. A.; Farnham, W. B.; Smart, B. E. *Inorg. Chem.* **1990**, *29*, 2954.

Table 3. Bond Lengths (pm) and Angles (deg) in the Anion of $(CH_3)_4N^+OCFCF_2O^-$ from X-ray Measurements and *ab Initio* Calculations

| | X-ray | DZP+diff[a] | 6-31+G(d,p)[b] | DFT[c] | F₂ in a fixed position | |
					6-31+G(d,p)[b]	DFT[c]
C1−C2	153.2(2)	155.6	155.8	156.3	155.3	156.7
C1−F2	148.0(2)	140.8	141.2	148.2	(148.0 fixed)	
C1−F3	141.3(2)	140.8	141.2	148.2	139.0	146.5
C1−O1	122.0(2)	122.3	122.1	122.6	121.6	122.7
C2−O2	117.2(2)	117.2	117.0	119.3	117.0	119.3
C2−F1	135.2(2)	133.5	133.9	138.1	133.6	138.5
O1−C1−F2	114.6(2)	116.1	116.0	116.0	115.5	116.2
O1−C1−F3	115.9(2)	116.1	116.0	116.0	116.7	116.0
O1−C1−C2	119.2(2)	117.3	117.2	118.6	118.0	118.6
F2−C1−C2	98.3(1)	102.0	102.0	101.6	(98.3, fixed)	
F3−C1−C2	106.5(1)	102.0	102.0	101.6	105.2	104.3
F2−C1−F3	99.4(1)	100.9	100.8	100.0	100.3	100.3
F1−C2−C1	112.79(1)	112.8	112.9	113.5	113.3	113.8
O2−C2−C1	127.0(2)	128.4	128.4	128.2	127.8	127.9
O2−C2−F1	120.1	118.4	118.7	118.3	118.0	118.2
O1−C1−C2−O2	−17.9(3)		0.0	0.0	−18.5	−19.7
F3−C1−C2−O2	−151.2(2)		−128.0	−128.5	−150.6	−150.8
F2−C1−C2−O2	106.3(2)		+128.0	+128.5	(106.3 fixed)	
O1−C1−C2−F1	166.3(2)		180.0	180.0	163.6	162.3
tot energy (au)		−523.97247	−523.85202	−526.29887	−523.85039	−526.29835

[a] Data from ref 21: double ζ basis set with d polarization and diffuse p functions. [b] This work: restricted Hartree−Fock calculation with Gaussian 6-31 basis set and polarization and diffuse functions. [c] This work: density functional calculation, same basis set as in footnote b, local and nonlocal electron correlation by the Becke 3 parameter functional[15] and the correction by Lee, Young, and Barr.[16]

In our study it is shown that COFCOF reacts quantitatively with $(CH_3)_4N^+F^-$ to form a colorless, but hygroscopic adduct, which is stable to 140 °C. The vibrational spectra are in agreement with the crystal structure described below but alone would not allow a precise conclusion about the anion structure. Interestingly, the ¹⁹F NMR spectrum shows only one broad signal, indicating complete fluorine exchange even at −40 °C.

The results of the crystal structure determination are shown in Table 3 and Figures 3 and 4. The anion has clearly a non-fluorine-bridged structure. It is close to the conformer **b** from the *ab initio* calculation, where the two oxygen atoms are eclipsed. This has been calculated to be the second best conformation, which differs by only 2.0 kJ/mol (0.5 kcal/mol) from conformation **a**.[21]

Discussion

The structures of the anions in $[(CH_3)_2N]_3S^+CF_3O^-$,[21] $pip^+CF_3CF_2O^-$, and $pip^+(CF_3)_2CFO^-$ allow a detailed discussion of the influence of the negative hyperconjugation. In all three cases the carbon oxygen bond length is much shorter than the length of the adjacent carbon fluorine bond. Also bond angles that contain the oxygen atom are always larger than the tetraedral angle 109°, paralleled by smaller than 109° angles if the adjacent fluorine atom is involved; see Table 2. The crystal structure data for CF_3O^- and $CF_3CF_2O^-$ are well reproduced by the *ab initio* calculations, except that all bond lengths come out larger by a few picometer. These findings indicate that the negative hyperconfiguration plays a significant role in these anions. This becomes particularly obvious if the C−O bond lengths of $CF_3CF_2O^-$ is compared to those in $CF_3CH_2O^-$. Data for $CF_3CH_2O^-$ are obtained from an adduct containing $[CF_3CH_2O]_4$, which has four C−O bond lengths between 139.7 and 141.9 pm.[22] While the C−O bond lengths in CF_3O^- and $CF_3CF_2O^-$ are very much alike, the C−F bonds of the two adjacent fluorine atoms in $CF_3CF_2O^-$ are markedly longer than the three bonds in CF_3O^-. So one can arrive at the conclusion that the negative hyperconjugation is even more pronounced in $CF_3CF_2O^-$ than in CF_3O^-.

This trend cannot be extrapolated to $(CF_3)_2CFO^-$, however. Already the *ab initio* calculation predicts a little longer C−O

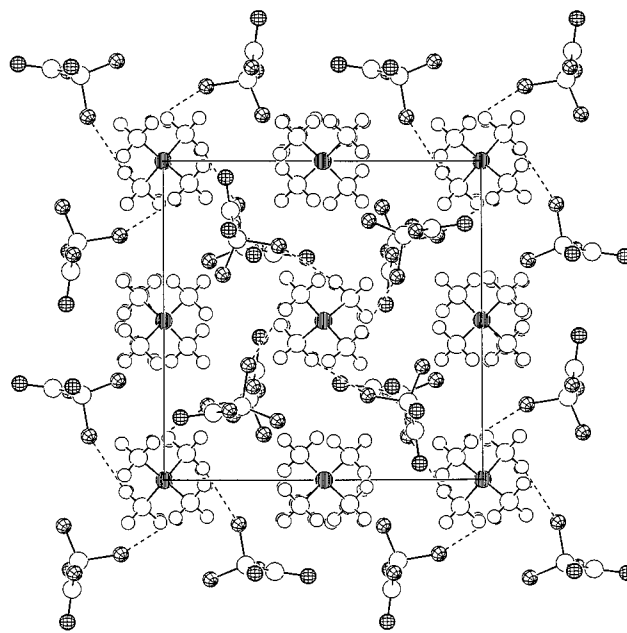**Figure 4.** XP plot showing the packing of $(CH_3)_4N^+FCOCF_2O^-$, viewed along the tetragonal axis. The contact F2···H of 237 pm is indicated by dotted lines.

bond and a little shorter C−F bond then in CF_3CFO^- or CF_3O^-. In the solid state this difference becomes dramatic: The C−O bond (134.3 pm) is only a little shorter than the C−F bond (141.6 pm). The C−O bond is not very much different from the C−O bonds found in $(CF_3)_2CHO^-$, which vary between 135.2 and 136.2 pm in $[CF_3CH_2ONa]_4$.[23]

In search for an explanation for the surprisingly long C−O bond in $(CF_3)_2CFO^-$, we observe four contacts of the oxygen atom to hydrogen atoms of the cations of 231, 247, 248, and 257 pm length, whereas in $CF_3CF_2O^-$ the oxygen atom has only three such contacts of 247, 251, and 254 pm length. It is interesting to note that the hydrogen atoms involved in such contacts to oxygen are all α-hydrogen with respect to the

(23) Rothfurs, H.; Folting, K.; Caulton, K. G. *Inorg. Chim. Acta* **1993**, *212*, 165.

nitrogen atom of the 1,1,3,3,5,5-piperidinium ion, which indeed can be assumed to carry most of the positive charge of the cation. It is therefore indicated that the oxygen atom of (CF$_3$)$_2$CFO$^-$ carries more negative change than the oxygen atom in CF$_3$CF$_2$O$^-$. But it is not possible to say whether different negative charge by different negative hyperconjugation gives rise to different O⋯H contact, both in length and number, which then influences the packing of cations and anions in the crystal, or whether on the contrary different crystal packing results in different O⋯H contacts, which then may cause different charges on the two oxygen atoms in CF$_3$CF$_2$O$^-$ and (CF$_3$)$_2$CFO$^-$.

The anion COFCF$_2$O$^-$ seems to have structure **b**. Nevertheless the found structure deviates from this idealized conformer quite remarkably. As can be seen from Figure 3, the anion is made up from a nearly planar COFCOF frame work, with an additional fluorine atom F2, situated almost perpendicular to this plane with a rather long distance to C2 of 148.0(2) pm. The C−C−F(2) angle of this fluorine atom is also much smaller (98.3)° than the C−C−F(3) angle (106.5°) of the second fluorine atom at C2. The fluorine atom seems to have moved somewhat into a bridging position.

The origin of this irregular structure cannot be traced to the free anion, since calculations with varying basis sets including electron correlation,[16,17] starting with the experimental geometry, always optimized to C_s geometry with equal C2−F bond lengths

and angles. From the packing diagram, see Figure 4, it can be seen that F2 has one particularly short contact (237 pm) to one hydrogen atom of the cation, whereas contacts of the other oxygen and fluorine atoms are in the vicinity of 260−270 pm. Therefore, we conclude that weak interionic forces drive the anion into this peculiar structure. In order to simulate the influence of this cationic−anionic interaction, the structure of the anion was calculated with a 6-31+G(d,p) basis set with and without electron correlation by fixing the F2 position in the experimental position; see Table 3. The resulting structure resembles the experimental structure; especially, the shortening of the C1−F3 bond and the increase in the F3−Cl−C2 angle are well reproduced. This structure is calculated to be only 4.2 kJ/mol higher in energy than the structure of the free anion. If electron correlation is included, this energy difference decreases to 1.6 kJ/mol.

Concerning the discussion about negative hyperconjugation, it is also evident that not only fluorine atoms F2 but also F3 have long C−F bonds, and the C−O1 bond length (122.1 pm) is also indicative of this effect.

Supporting Information Available: Three X-ray crystallographic files, in CIF format, are available. Access information is given on any current masthead page.

(24) Samuels, J. A.; Lobkovsky, E. B.; Streib, W. E.; Folting, K.; Huffman, J. C.; Zwanziger, J. W.; Caulton, K. G. *J. Am. Chem. Soc.* **1993**, *115*, 5093.