Synthesis and Characterization of Novel Iodine(III) Compounds; Crystal Structures of Methoxy(trifluoromethyl)iodine(III) Chloride [$CF_3I(Cl)OCH_3$] and Dimethoxy(trifluoromethyl)iodine(III) [$CF_3I(OCH_3)_2$]

Rolf Minkwitz,*[a] Michael Berkei,[a] and Ralf Ludwig[a]

Keywords: Iodine / Structure elucidation / Vibrational spectroscopy

The reactions of $CF_3I(Cl)F$ and CF_3IF_2 with $(CH_3)_3SiOCH_3$ lead to the novel iodine(III) compounds $CF_3I(Cl)OCH_3$ and $CF_3I(OCH_3)_2$, respectively. The crystal structure of $CF_3I(Cl)OCH_3$ confirms that it is a ternary, trifluoromethyl-substituted iodine(III) derivative. $CF_3I(Cl)OCH_3$ crystallizes in the triclinic space group $P\bar{1}$, with four formula units per unit cell with the dimensions $a = 8.164(1)$, $b = 8.802(1)$, $c = 10.237(1)$ Å and angles $\alpha = 97.10(1)°$, $\beta = 91.41(1)°$, $\gamma = 115.00(1)°$. $CF_3I(OCH_3)_2$ crystallizes in the monoclinic space group $P2_1/n$ with four formula units per unit cell with $a = 6.295(1)$, $b = 15.607(1)$, $c = 7.736(1)$ Å, and $\beta = 111.44(1)°$. Both molecules have been additionally characterized by Raman, IR, and NMR spectroscopy and the experimental results are compared with quantum-mechanically calculated parameters.

Introduction

The chemistry of (trifluoromethyl)iodine(III) compounds is a well-explored field of research, although crystal structures have been obtained in only a few cases. The reported structures are limited to compounds having highly electronegative ligands, such as F, Cl, or ONO_2, in the apical positions.[1−3] These compounds are more stable and can be isolated more easily than derivatives having less electronegative ligands. According to Bent's rule, the apical positions are favourably occupied by the most electronegative ligands.[4] These positions are characterized by 3-center-4-electron bonds, in which the negative charge is located at the termini.[5]

Since all attempts to synthesize $CF_3I(OH)_2$ have proven unsuccessful, we became interested in its alkyl-substituted derivatives $CF_3I(OR)_2$. The tendency of iodine to form double bonds with oxygen leads to destabilization of these compounds and favours condensation reactions leading to CF_3IO. Although methanolysis of PhIO leads to $PhI(OCH_3)_2$ and Naumann et al. supposed a similar tendency of CF_3IO to form $CF_3I(OCH_3)_2$, no experimental details of this have yet been reported.[6,7] In 1974, Oates and Winfield described the synthesis of $CF_3IF_{4-n}(OCH_3)_n$ ($n = 1-4$) by reaction of CF_3IF_4 with $(CH_3)_3SiOCH_3$.[8] All the products were identified by their mass and NMR spectra. Since no similar investigation has been carried out in the case of iodine(III), it seemed desirable to study the reaction of CF_3IF_2 with $(CH_3)_3SiOCH_3$. In this reaction, $CF_3I(F)OCH_3$ is expected to be an observable intermediate. In general, ternary iodine(III) compounds are known to decompose by symmetrization in solution, even at low temperatures, and are thus difficult to isolate.[9] In order to obtain ternary iodine(III) compounds, $CF_3I(Cl)F$ represents a good starting material.[9] In this compound, the I−F bond is elongated and the I−Cl bond is shortened. This renders it suitable for exchange reactions in which only the I−F bond is replaced.

In this work, we report the syntheses and crystal structures of $CF_3I(Cl)OCH_3$ and $CF_3I(OCH_3)_2$. As far as we are aware, this constitutes the first report of structural data for (trifluoromethyl)iodine(III) compounds substituted by methoxy groups.

Results and Discussion

Formation of $CF_3I(Cl)OCH_3$ and $CF_3I(OCH_3)_2$

The molecules were obtained by reactions of (methoxy)-trimethylsilane with $CF_3I(Cl)F$ and CF_3IF_2, respectively [Equations (1) and (2)]. This synthesis is analogous to the preparation of $CF_3IF_n(OCH_3)_{4-n}$ ($n = 1-4$) by Oates and Winfield.[8] The driving force behind these reactions is the formation of the thermodynamically favoured Si−F bond at the expense of the Si−O bond.

$$CF_3I(Cl)F + (CH_3)_3SiOCH_3 \xrightarrow{-80°C} CF_3I(Cl)OCH_3 + (CH_3)_3SiF$$

$$CF_3IF_2 + 2(CH_3)_3SiOCH_3 \xrightarrow{-50°C} CF_3I(OCH_3)_2 + 2(CH_3)_3SiF$$

The fine colourless solids proved to be stable for several months at −70 °C under nitrogen, decomposing at about −40 °C. The iodine(III) compounds were found to be soluble in sulfur dioxide at −50 °C. In solution, they start to decompose even at temperatures below −50 °C.

Vibrational Spectra

The observed Raman and IR frequencies of $CF_3I(Cl)OCH_3$ and $CF_3I(OCH_3)_2$ are summarized in

[a] Fachbereich Chemie der Universität Dortmund, 44221 Dortmund, Germany

  1434−1948/00/1111−2387 $ 17.50+.50/0

Table 1. The vibrational spectra are assigned on the basis of C_1 symmetry for the molecules. For $CF_3I(Cl)OCH_3$, 27 fundamental vibrations are to be expected. The strongest line in the Raman spectrum at 509 cm^{-1} corresponds to the I−O stretching mode. The I−Cl stretching mode can be assigned to the line at 304 cm^{-1}. This is in good accordance with assignments made for $CF_3I(Cl)ONO_2$ (326 cm^{-1}) and $CF_3I(Cl)F$ (304 cm^{-1}).[3,9] The asymmetric CF_3 stretching modes are found in the range 1056 to 1209 cm^{-1}, while the symmetric mode is seen at about 1043 cm^{-1}. The corresponding bending modes are observed at 739 cm^{-1} (δ_{as} CF_3), 542 cm^{-1} (δ_s CF_3), and in the range 243 to 265 cm^{-1} (ρ CF_3). In the case of $CF_3I(OCH_3)_2$, the I−O stretching modes can be assigned to the strongest lines in the Raman spectrum at 532 cm^{-1} (ν_{as} IO_2) and 353 cm^{-1} (ν_s IO_2), respectively, while the IO_2 bending is seen at 236 cm^{-1}. For comparison, in $CF_3I(ONO_2)_2$, these vibrational modes are found at 705−734 cm^{-1} (ν_{as} IO_2), 332/346 cm^{-1} (ν_s IO_2), and 182/190 cm^{-1} (δ IO_2).[3] The C−I stretching mode is observed at about 277 cm^{-1}. The vibrational bands of the CF_3 and CH_3 groups were detected in the expected ranges.

Table 1. Vibrational frequencies of $CF_3I(Cl)OCH_3$ and $CF_3I(OCH_3)_2$

$CF_3I(Cl)OCH_3$ Raman $T = -196$ °C	IR[a] $T = -50$ °C	$CF_3I(OCH_3)_2$ Raman $T = -196$ °C	IR[a] $T = -50$ °C	Assignment
2994 (12)[b]		3001 (41)[b]		ν_{as} CH_3
2984 (14)		2965 (29)	2961 w	ν_{as} CH_3
2978 (12)		2947 (33)	2943 w	ν_{as} CH_3
2957 (11)	2960 w	2917 (21)	2918 w	ν_{as} CH_3
2938 (15)				ν_{as} CH_3
2898 (11)		2903 (23)		ν_{as} CH_3
2825 (12)	2821 vw	2838 (41)	2835 w	ν_s CH_3
1929 (8)			1971 vw	
1465 (8)	1461 w	1458 (19)	1457 m	δ_{as} CH_3
1459 (9)				δ_{as} CH_3
1449 (9)				δ_{as} CH_3
1440 (9)			1443 m	δ_{as} CH_3
1437 (9)	1434 w			δ_{as} CH_3
1430 (9)		1416 (9)		δ_{as} CH_3
			1288 w	δ_s CH_3
	1255 m		1255 w	δ_s CH_3
1209 (8)	1201 vs	1210 (9)	1201 vs	ν_{as} CF_3
1196 (8)				ν_{as} CF_3
1194 (8)		1175 (9)	1187 s	ν_{as} CF_3
1165 (9)		1160 (10)		ν_{as} CF_3
1156 (8)		1097 (10)		ν_{as} CF_3
1045 (14)	1042 vs	1075 (14)		ν_s CF_3
		1060 (19)	1054 vs	ν_s CF_3
			1018 m	ν CO
977 (18)	968 m	997 (25)	989 s	ν CO
	844 m		849 w	
	821 sh	817 (29)	820 m	
739 (33)	738 s	745 (59)	740 s	δ_s CF_3
		548 (33)		δ_{as} CF_3
542 (10)		542 (81)		δ_{as} CF_3
530 (10)		532 (100)	536 s	ν_{as} IO_2
		513 (24)	517 m, sh	
508 (100)	510 m			ν IO
		411 (22)	407 m	
		353 (85)	360 s	ν_s IO_2
313 (13)	329 w	329 (31)	324 m	δ ClO
			310 m	
304 (17)	304 m			ν ICl
		290 (36)		
		285 (47)		
278 (18)	279 w	279 (56)	274 m	ν CI
265 (59)	266 w	266 (26)	264 vw	ρ CF_3
243 (35)		254 (26)		ρ CF_3
		236 (15)	238 w	δ IO_2
215 (52)				δ ClCl
		210 (15)		
149 (20)				δ OICl
137 (23)		128 (24)		lattice modes
118 (13)		113 (27)		lattice modes
92 (23)				lattice modes
79 (20)				lattice modes
62 (25)				lattice modes

[a] vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder. − [b] Relative intensities are given in parentheses.

Crystal Structure of $CF_3I(Cl)OCH_3$

$CF_3I(Cl)OCH_3$ crystallizes in the triclinic space group $P\bar{1}$ with four formula units per unit cell. The crystal data are summarized in Table 2. The molecule has a distorted Ψ-trigonal bipyramidal structure with chlorine and the methoxy group in the apical positions and the trifluoromethyl group and two lone pairs in the equatorial positions (Figure 1). This is in accordance with the Gillespie−Nyholm model and the structure can be described as T-shaped.[10,11] Bond lengths and selected bond angles are listed in Table 3.

The unit cell contains two crystallographically independent molecules with slightly different bond lengths. The I−Cl bonds have lengths of 2.578(2) and 2.580(2) Å, about 0.3 Å longer than the sum of the covalent radii, and are 0.1 Å longer than those found in CF_3ICl_2.[2,12] For the I−O bonds, values of 1.969(5) and 1.991(5) Å are observed, these being only slightly longer than the sum of the covalent radii of 1.94 Å.[12] The molecules are arranged in chains, due to strong intermolecular I−Cl contacts. Owing to intermolecular I−O contacts, the chains are arranged in layers, stacked along the *b* axis. All these interactions result in the formation of ribbons of twelve-membered, centrosymmetric rings (Figure 1). In these rings, I−O−I−O parallelograms are spanned by two molecules involving I−O contacts with lengths of 3.235(5) and 3.250(5) Å. On the basis of these contacts, the environment at the iodine atom can be designated as distorted square-pyramidal. Between the layers of molecules, no contacts shorter than the sum of the van der Waals radii are found.

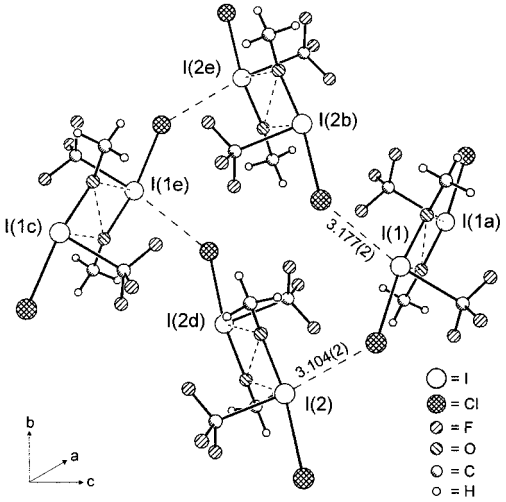

Figure 1. Fragment of the structure of $CF_3I(Cl)OCH_3$; projection of a twelve-membered ring; distances [Å]: I(1)···Cl(2b) 3.177(2), I(1)···O(1a) 3.235(5), O(1)···O(1a) 2.864(5), I(2)···Cl(1) 3.104(2), I(2)···O(2d) 3.250(5), O(2)···O(2d) 2.878(5); symmetry operations: *a*: $-x+2, -y+1, -z+1$; *b*: $x+1, y, z$; *c*: $x, y, z-1$; *d*: $-x+1, -y+1, -z$; *e*: $-x+2, -y+1, -z$

Crystal Structure of $CF_3I(OCH_3)_2$

$CF_3I(OCH_3)_2$ (Figure 2) crystallizes in the monoclinic space group $P2_1/n$ with four formula units per unit cell. The crystal data are summarized in Table 2 and bond lengths and selected angles are listed in Table 3. $CF_3I(OCH_3)_2$ has a T-shaped arrangement with two methoxy groups in apical positions. The I−O bonds have lengths of 2.019(11) Å

Table 2. X-ray diffraction data of $CF_3I(Cl)OCH_3$ and $CF_3I(OCH_3)_2$

	$CF_3I(Cl)OCH_3$	$CF_3I(OCH_3)_2$
Space group	$P\bar{1}$	$P2_1/n$
Crystal system	triclinic	monoclinic
a [Å]	8.164(1)	6.295(1)
b [Å]	8.802(1)	15.607(1)
c [Å]	10.237(1)	7.736(1)
α [°]	97.10(1)	90
β [°]	91.41(1)	111.44(1)
γ [°]	115.00(1)	90
Volume [Å^3]	659.17(13)	707.4(2)
Density (calcd.) [g cm^{-3}]	2.644	2.422
Z	4	4
Molecular mass [g mol^{-1}]	262.39	257.98
Absorption coefficient [mm^{-1}]	5.231	4.516
Temperature [K]	173(2)	173(2)
F(000)	480	480
Wavelength [Å]	0.71069	0.71069
θ range for data collection [°]	$3.41 \le \theta \le 30.24$	$2.61 \le \theta \le 29.28$
Index ranges	$-11 \le h \le 9$	$-8 \le h \le 8$
	$-9 \le k \le 11$	$-19 \le k \le 19$
	$-14 \le l \le 11$	$-6 \le l \le 7$
Reflections collected/independent	3913/2401	3575/1316
	[*R*(int) = 0.0418]	[*R*(int) = 0.1469]
Parameters	145	82
Goodness-of-fit on F^2	1.031	1.015
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0421	*R*1 = 0.0672
	*wR*2 = 0.0989	*wR*2 = 0.1549
R indices (all data)	*R*1 = 0.0629	*R*1 = 0.1372
	*wR*2 = 0.1087	*wR*2 = 0.1977
Largest diff. peak and hole [e$^-$ Å^{-3}]	1.757 and −1.619	1.187 and −1.018
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2

Table 3. Quantum-mechanically calculated bond lengths [Å] and angles [°] in $CF_3I(Cl)OCH_3$ and $CF_3I(OCH_3)_2$ in comparison with the experimentally observed values

	$CF_3I(Cl)OCH_3$				$CF_3I(OCH_3)_2$		
	exp.	RHF-LANL2DZ	B3LYP-LANL2DZ		exp.	RHF-LANL2DZ	B3LYP-LANL2DZ
I1−Cl1	2.578(2)	2.6559	2.6806	I1−O1	2.019(11)	2.0154	2.1106
I2−Cl2	2.580(2)	2.6559	2.6806	I1−O2	2.087(11)	2.0268	2.1106
I1−O1	1.969(5)	1.9843	2.0996	I1−C3	2.190(12)	2.1846	2.2896
I2−O2	1.991(5)	1.9843	2.0996	O1−C1	1.40(2)	1.4338	1.4580
I1−C1	2.212(8)	2.2054	2.2815	O2−C2	1.38(2)	1.4334	1.4580
I2−C2	2.207(7)	2.2054	2.2815	ø C−F[a]	1.31(2)	1.3569	1.3876
O1−C4	1.443(7)	1.4465	1.4674				
O2−C3	1.450(8)	1.4465	1.4674				
ø C−F[a]	1.311(8)	1.3495	1.3786				
Cl1−I1−O1	171.0(2)	170.06	171.22	O1−I1−O2	166.7(4)	165.28	169.05
Cl2−I2−O2	171.0(2)	170.06	171.22	O1−I1−C3	81.4(5)	86.11	84.61
Cl1−I1−C1	81.7(2)	81.68	83.35	O2−I1−C3	85.3(5)	79.41	84.61
Cl2−I2−C2	82.0(2)	81.68	83.35	C1−O1−I1	115.0(10)	129.95	120.29
C1−I1−O1	89.3(3)	88.43	88.34	C2−O2−I1	117.0(9)	129.01	120.29
C2−I2−O2	89.2(2)	88.43	88.34				
I1−O1−C4	116.4(4)	126.67	119.48				
I2−O2−C3	113.9(4)	126.67	119.48				

[a] For the sake of simplicity, the average C−F bond lengths are shown.

[I(1)−O(1)] and 2.087(11) Å [I(1)−O(2)] and are significantly longer than the sum of the covalent radii of 1.94 Å and the corresponding bonds in $CF_3I(Cl)OCH_3$ [1.969(5) and 1.991(5) Å].[12] The molecules present donors as well as acceptors for each secondary I−O bond, which points to the C−I bond. For iodine, a square-planar environment results. Taking the intermolecular contacts into consideration, the observed difference in I−O bond lengths due to weakening of the I(1)−O(2) bond becomes reasonable. The molecules are arranged in chains along the *c* axis. The CF_3 group and the methoxy group of O(1) are not involved in any intermolecular contacts and occupy the positions of side groups on the chains. A similar arrangement is found in CF_3ICl_2.[2] The C−I distance of 2.190(12) Å is comparable to those in similar compounds such as CF_3IF_2 [2.174(6) Å], CF_3ICl_2 [2.229(10) Å], and $CF_3I(ONO_2)_2$ [2.212(4) Å].[1−3] The CF_3 group is almost tetrahedral with F−C−F angles of about 108° and an average C−F bond length of about 1.31(2) Å.

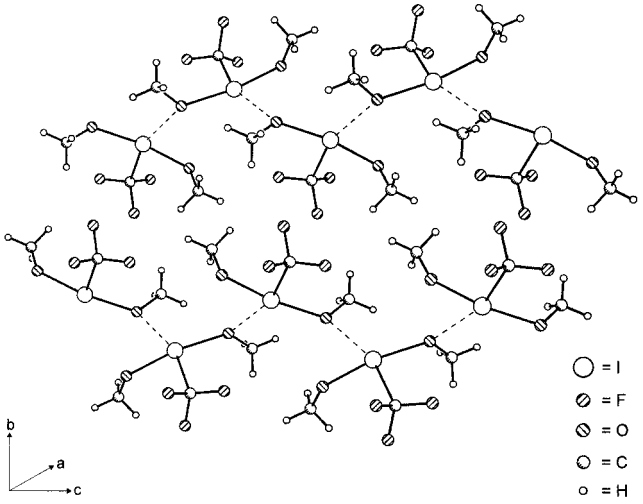

Figure 2. View of the crystal structure of $CF_3I(OCH_3)_2$ in *q* orientation; the intermolecular I−O contacts measure 2.749(9) Å

Quantum-Mechanical Calculations

Ab initio RHF and density functional B3LYP calculations were performed using the Gaussian 98 program.[13] To take relativistic effects into account, calculations were carried out with the LANL2DZ basis set, which includes D95 on first-row atoms, and a Los Alamos ECP, which puts DZ on other atoms.[14−17] Additional calculations with CEP-121G and SDD basis sets not described here yielded similar results.[18−21] To obtain optimized molecular structures, the wavefunctions were analyzed by the natural bond orbital (NBO) method, a standard program option of Gaussian 98.[22]

The optimized geometries for both systems are given in Table 3 and are compared with experimental data. Whereas the HF method overestimates the I−Cl bond length by about 8 pm, the density functional method B3LYP systematically overestimates the lengths of all iodine-containing bonds by about 10 pm. With the chosen basis set, the B3LYP approximation does not yield adequate results for iodine-containing systems. It should also be borne in mind that all calculations were performed for free molecules in the gas phase. Some deviations between the calculated and experimentally observed values can thus be attributed to the strong intermolecular cross-links in the crystalline solid state. In the case of $CF_3I(OCH_3)_2$, we could not find any explanation for the difference in symmetries calculated by the two methods.

For both compounds, NBO analyses for all methods and basis sets were performed.[22] Summarizing the calculated charges on each atom of the various ligands clearly indicates that total negative charges increase in the order: $F_3C > H_3CO > Cl$ (Table 4). The calculated charges support the assumption that the apical ligands are bound by 3-center-4-electron bonds.[5] In 1992, Boyd and Boyd reported group electronegativities calculated by the bond critical model.[23] For the CF_3 and H_3CO groups, values of 2.71 and 3.53, respectively, were calculated.[23] In accordance with Bent's

rule, this explains the apical positions of chlorine and the methoxy group in $CF_3I(Cl)OCH_3$ and of both methoxy groups in $CF_3I(OCH_3)_2$.[4]

Table 4. Calculated and summarized NBO charges of the three different ligands in $CF_3I(Cl)OCH_3$ and $CF_3I(OCH_3)_2$; charges are given in e^-

	$CF_3I(Cl)OCH_3$		$CF_3I(OCH_3)_2$	
	RHF LANL2DZ	B3LYP LANL2DZ	RHF LANL2DZ	B3LYP LANL2DZ
Cl	−0.472	−0.616		
H_3CO	−0.420	−0.545	−0.494	−0.641
F_3C	−0.112	−0.132	−0.210	−0.215

Experimental Section

Caution! $CF_3I(Cl)F$ and CF_3IF_2 are unstable at room temperature and are sensitive to moisture. Skin contact with these compounds should be avoided because their hydrolysis leads to HF or HCl, which cause burns and in some cases irreparable damage. Safety precautions should be taken when using and handling these materials.

All synthetic work and sample handling was performed using a standard glass vacuum line and standard Schlenk techniques. Nonvolatile materials were handled under dry nitrogen. The syntheses of $CF_3I(Cl)F$ and CF_3IF_2 were carried out by treating trifluoromethyl iodide (CF_3I) with trifluoromethyl hypochlorite (CF_3OCl) at −78 °C and −50 °C, respectively, based on literature methods.[1,9] (Methoxy)trimethylsilane [$(CH_3)_3SiOCH_3$] (ABCR) was used as received without any purification. Owing to the low stability of the products, we were unable to obtain reliable elemental analysis results. − The Raman spectra were recorded with a Jobin Yvon T64000 spectrometer using an Ar^+ laser (514.5 nm) from Spectra Physics. The spectra were obtained from samples in a glass cell cooled with liquid N_2.[24] − Infrared spectra were recorded with a Bruker IFS 113v spectrophotometer. Spectra were obtained from samples coated on CsBr plates placed in a low-temperature cell.[25] − NMR spectra in SO_2 solution at −50 °C were recorded with Bruker DPX 300 and Bruker DRX 400 spectrometers. − Single crystals were placed in Lindemann capillaries in a cooled stream of dry nitrogen, and X-ray diffraction data were collected using a Nonius Kappa CCD diffractometer. The crystal structures were solved by the Patterson method and successive difference Fourier syntheses. For refinement, full-matrix least-squares methods were applied. Data reduction, structure solution, and refinement were carried out with programs in the SHELXTL package, PLATON, MISSYM, and PARST.[26−30]

Quantum-Mechanical Calculations: Hartree−Fock and density functional calculations were performed with the program Gaussian 98.[13] In the density functional B3LYP,[31] the 3-parameter exchange functional by Becke[32] and the correlation functional by Lee, Yang, and Parr[33] were used. The LANL2DZ basis set contains a D95 basis[14] for elements of the first period and an effective core potential and a double-zeta basis for elements from sodium to bismuth.[15−17] For the geometry optimization, different starting coordinates were chosen. The calculation of the vibrational frequencies showed whether or not the energy-minimized structures represented stable molecules. All frequencies were positive, indicating that at least local minima on the Born−Oppenheimer hypersurface were found.

Preparation of $CF_3I(Cl)OCH_3$: In a typical reaction, $(CH_3)_3SiOCH_3$ (0.26 g, 2.50 mmol) was condensed onto $CF_3I(Cl)F$ (0.50 g, 2.00 mmol) in a dry glass vessel with greaseless stopcocks (Young). The mixture was then allowed to warm to −80 °C and was maintained at this temperature for 30 min. After removal of the volatile materials in vacuo at −70 °C, the formation of 0.39 g (1.49 mmol, 74%) of methoxy(trifluoromethyl)iodine(III) chloride, $CF_3I(Cl)OCH_3$, was observed. The resulting colourless solid was found to be stable up to −40 °C and sensitive to moisture. − NMR: ^{19}F: δ = −29.68 (s, CF_3). − ^{13}C: δ = 67.47 (s, CH_3), 83.09 (q, ^1J = 344 Hz, CF_3). − ^1H: δ = 4.13 (s, CH_3).

Preparation of $CF_3I(OCH_3)_2$: $(CH_3)_3SiOCH_3$ (0.52 g, 5.00 mmol) was condensed onto CF_3IF_2 (0.47 g, 2.00 mmol) in a dry glass vessel with greaseless stopcocks (Young). The mixture was allowed to warm to −50 °C and was maintained at this temperature for 1 h. After removal of the volatile materials in vacuo at −50 °C, the formation of 0.24 g (0.93 mmol, 48%) of dimethoxy(trifluoromethyl)iodine(III), $CF_3I(OCH_3)_2$, was observed. The resulting colourless solid was found to be stable up to −40 °C and sensitive to moisture. − NMR: ^{19}F: δ = −28.42 (s, CF_3). − ^{13}C: δ = 63.21 (s, CH_3), δ = 81.19 (q, ^1J = 344 Hz, CF_3). − ^1H: δ = 4.36 (s, CH_3).

Acknowledgments

This work was supported by the Fonds der Chemischen Industrie.

[1] R. Minkwitz, M. Berkei, *Inorg. Chem.* **1998**, *37*, 5247−5250.
[2] R. Minkwitz, M. Berkei, *Inorg. Chem.* **1999**, *38*, 5041−5044.
[3] R. Minkwitz, T. Hertel, H. Preut, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1552−1557.
[4] H. A. Bent, *Chem. Rev.* **1961**, *61*, 275−311.
[5] A. Varvoglis, in *The Organic Chemistry of Polycoordinated Iodine*, VCH, Weinheim, **1992**, p. 1−119.
[6] J. F. Kinneary, J. S. Albert, C. J. Burrows, *J. Am. Chem. Soc.* **1988**, *110*, 6124−6129.
[7] D. Naumann, L. Deneken, E. Renk, *J. Fluorine Chem.* **1975**, *5*, 509−519.
[8] G. Oates, J. M. Winfield, *J. Chem. Soc., Dalton Trans.* **1974**, 119−124.
[9] R. Minkwitz, R. Bröchler, M. Schütze, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1727−1730.
[10] R. J. Gillespie, R. S. Nyholm, *Quart. Rev., Chem. Soc.* **1957**, *11*, 339−380.
[11] R. J. Gillespie, *J. Chem. Educ.* **1963**, *40*, 295−301.
[12] A. Bondi, *J. Phys. Chem*. **1964**, *68*, 441−451.
[13] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98 (Revision A.1)*, Gaussian, Inc., Pittsburgh PA, **1998**.
[14] T. H. Dunning, Jr., P. J. Hay, in *Modern Theoretical Chemistry* (Ed.: H. F. Schaefer, III), Plenum, New York, **1976**, p. 1−28.
[15] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270−283.
[16] W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284−298.
[17] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299−310.
[18] W. Stevens, H. Basch, J. Krauss, *J. Chem. Phys.* **1984**, *81*, 6026−6033.
[19] W. J. Stevens, J. Krauss, H. Basch, P. G. Jasien, *Can. J. Chem.* **1992**, *70*, 612−630.
[20] T. R. Cundari, W. J. Stevens, *J. Chem. Phys.* **1993**, *98*, 5555−5565.

[21] U. Wedig, M. Dolg, H. Stoll, H. Preuss, in *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry* (Ed.: A. Veillard), Reidel, Dordrecht, **1986**, p. 79.

[22] A. E. Reed, L. A. Curtis, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899−926.

[23] R. J. Boyd, S. L. Boyd, *J. Am. Chem. Soc.* **1992**, *114*, 1652−1655.

[24] A. Werner, Dissertation, University of Dortmund, Germany, **1988**.

[25] L. Bayersdorfer, R. Minkwitz, J. Jander, *Z. Anorg. Allg. Chem.* **1972**, *392*, 137−142.

[26] G. M. Sheldrick, *SHELXTL-PLUS: An Integrated System for Solving, Refining, and Displaying Structures from Diffraction Data*, University of Göttingen, Germany, **1987**.

[27] A. L. Spek, "The EUCLID Package", in *Computational Crystallography* (Ed.: D. Sayre), Clarendon Press, Oxford, **1982**, p. 528.

[28] Y. Le Page, *J. Appl. Crystallogr.* **1987**, *20*, 264−269.

[29] M. Nardelli, *Comput. Chem.* **1983**, *7*, 95−98.

[30] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-141229 [$CF_3I(Cl)OCH_3$] and -141228 [$CF_3I(OCH_3)_2$]. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[31] B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200−206.

[32] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648−5652.

[33] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785−789.

Received March 6, 2000
[I00089]