Inorg. Chem. **1998,** *37,* 5247−5250

A New Preparation and Crystal Structure of Trifluoromethyl Iodine Difluoride CF_3IF_2

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Received May 4, 1998

Trifluoromethyl iodine difluoride (CF_3IF_2) is synthesized by the reaction of trifluoromethyl iodide (CF_3I) with trifluoromethyl hypochlorite (CF_3OCl) at 223 K. This is a new route of preparation, in which CF_3I is fluorinated by CF_3OCl in an addition−elimination reaction. CF_3IF_2 crystallizes in the tetragonal space group $I\bar{4}2d$ with $a = 8.509(1)$ Å, $c = 12.324(2)$ Å, and eight formula units per unit cell. Its molecular structure is T-shaped with a disordered CF_3 group. The Raman and IR spectra are described.

Introduction

Trifluoromethyl iodine difluoride, CF_3IF_2, was first prepared in 1959 by Schmeisser and Scharf by fluorination of trifluoromethyl iodide, CF_3I.[1] It can be described as a trifluoromethyl-substituted derivative of iodine trifluoride, IF_3, and was the first iodine(III) compound to contain a trifluoromethyl group. Since then CF_3IF_2 has been synthesized in several ways. Rondestvedt found that perfluoroalkyl iodides can be oxidized by ClF_3, BrF_3, or BrF_5 to obtain R_fIF_2 and R_fIF_4.[2] This opened up a general way to prepare the group of perfluoroalkyl iodine fluorides in which iodine has the oxidation state +III or +V. The first spectroscopic data for CF_3IF_2 were reported by Chambers, Oates, and Winfield in 1972, when the ^{19}F NMR spectrum was recorded.[3] Schmeisser et al. improved the process of direct fluorination and described a general method for preparing perfluoroalkyl iodine fluorides in high quantity and purity.[4] In the following years, many reactions with CF_3IF_2 were carried out and reports of new iodine(III) compounds with different ligands followed.[5,6] In 1974 Naumann et al. reported the vibrational spectra of CF_3IF_2.[7] Their results suggest a trigonal bipyramidal structure with the two fluorine atoms in the apical position and the trifluoromethyl group in the equatorial position. They assumed that there are strong interactions between the CF_3IF_2 monomers and that the solid is mainly associated in the form of chains. A new way to prepare CF_3IF_2 was found by Naumann and Feist who fluorinated CH_3I with elemental fluorine under mild conditions to yield CF_3IF_2.[8]

Since no X-ray structure for IF_3 has yet been determined and there is a general lack of crystal structures of iodine(III) compounds containing fluorine ligands, there is great interest in the structure of CF_3IF_2. The usual ways of preparing CF_3IF_2 led only to amorphous powders, and efforts to recrystallize it from several solvents were unsuccessful. We therefore tried to find a new synthesis in order to obtain CF_3IF_2 in a crystalline form. Having experience with the chemistry of CF_3OCl, we attempted to use it as a mild fluorinating agent.[9−11] In 1995 we described the preparation and crystal structure of CF_3IF_4, prepared by reaction of CF_3I with CF_3OCl at a temperature of 243 K.[12] By varying the conditions of this reaction we obtained crystals of CF_3IF_2, and in this paper we report the crystal structure of CF_3IF_2 (Figure 1) and help to obtain answers for the structure of IF_3.

Experimental Section

Caution! *CF_3OCl and ClF are highly reactive oxidizing agents and are potential explosives when brought into contact with organic material. Avoid contact with these compounds because their hydrolyses form HF, which the skin burns and causes irreparable damage. Safety precautions should be taken when using and handling these materials.*

All synthetic work and sample handling were performed using a standard glass vacuum line and standard Schlenck techniques. Nonvolatile materials were handled under dry nitrogen. The synthesis of trifluoromethyl iodide (CF_3I) was carried out according to the literature method.[13] Trifluoromethyl hypochlorite (CF_3OCl) was prepared in a stainless steel vessel from CF_2O and ClF by using CsF as a catalyst.[14−16]

Infrared spectra were recorded on a Bruker IFS 113v spectrophotometer. Spectra of dry powders were obtained in a low-temperature cell with CsBr plates coated with the pure sample.[17] Raman spectra were recorded on a Jobin Yvon T64000 spectrometer by using an Ar^+ laser (514.5 nm, Spectra Physics). The spectra were recorded in glass cells cooled with liquid nitrogen or solid CO_2.[18] Single crystals were placed in Lindemann capillaries in a cooled stream of dry nitrogen, and an X-ray diffraction study was carried out with a Nonius Kappa CCD diffractometer.

Preparation of CF_3IF_2. CF_3OCl (0.60 g, 5 mmol) was condensed into a dry glass vessel with greaseless stopcocks (Young) onto 0.39 g (2 mmol) of CF_3I. The mixture was allowed to warm to 203 K and was then warmed to 223 K over a period of 24 h. At 203 K the formation of trifluoromethyl iodine chloride fluoride $CF_3I(Cl)F$ was

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S0020-1669(98)00503-5 CCC: $15.00

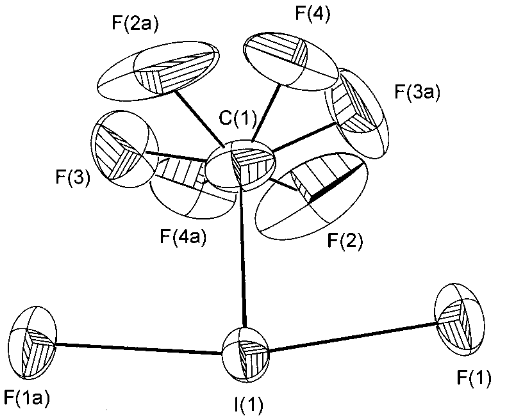
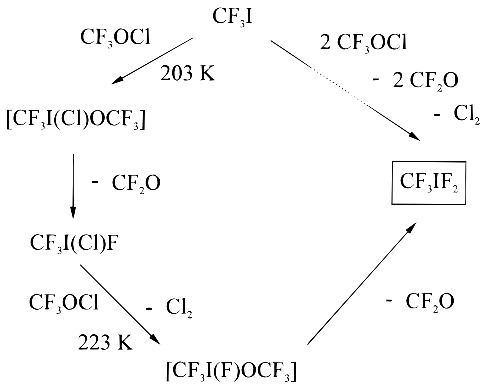


Figure 1. Projection of the CF_3IF_2 molecule. For symmetry transformations see Table 2. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 1. Path of the Reaction between CF_3I and CF_3OCl



observed.[19] When the sample was warmed up to 223 K this white solid dissolved, and after 24 h the volatile materials were removed at 183 K under vacuum. The resulting colorless crystals were stored under dry nitrogen at 203 K.

Results and Discussion

Reaction of CF_3I with CF_3OCl. The reaction between CF_3I and CF_3OCl is very complex, as shown in Scheme 1. It starts with the oxidative addition of CF_3OCl to iodine to form I^{III}. The resulting trifluoromethoxy-substituted compound cannot be isolated and yields $CF_3I(Cl)F$ with loss of CF_2O.[19] When the reaction mixture is warmed up to 223 K, this white solid dissolves and reacts with additional CF_3OCl under comproportionation with loss of Cl_2 and CF_2O to form CF_3IF_2. The driving force of this reaction is the formation of Cl_2 and CF_2O. After the volatile compounds are removed under vacuum, CF_3IF_2 remains as colorless crystals. It appears that the reaction mixture, which contains Cl_2, CF_2O, and excess CF_3OCl, is a suitable medium to crystallize this kind of molecule. In a similar reaction between CH_3I or CF_3I and $ClONO_2$, we also obtained $CH_3I(ONO_2)_2$, $CF_3I(Cl)ONO_2$, and crystals of $CF_3I(ONO_2)_2$.[20,21]

When the reaction temperature is raised to 243 K, CF_3IF_2 reacts with additional CF_3OCl to afford CF_3IF_4.[12] The mechanism for this reaction is the same as that described above. Higher temperatures lead to the cleavage of the C−I bond and the subsequent formation of IF_5.

This reaction is a good example of the synthetic potential of CF_3OCl, which can be used for addition reactions to unsaturated systems such as C=C double bonds. One example for these reactions is the preparation of trifluoromethyl-2,2-dichloroethyl ether, $CF_3OCH_2CCl_2H$, from CF_3OCl and vinyl chloride CH_2CHCl.[22] Trifluoromethyl hypochlorite is also suitable for comproportionation reactions with compounds containing negatively polarized chlorine: by using this type of reaction, Seppelt accomplished the synthesis of CF_3OH from HCl and CF_3OCl.[23] The third reaction type is oxidative addition, which was the starting point for our reaction. In contradiction to salts where stabilization is possible, the trifluoromethoxy group is usually not stable in neutral iodine compounds and converts under loss of CF_2O to the fluorine-substituted molecule.[19,24,25]

Crystal Structure of CF_3IF_2. CF_3IF_2 crystallizes in the tetragonal space group $I\bar{4}2d$ with $a = 8.509(1)$ Å, $c = 12.324(2)$ Å, and eight formula units per unit cell (Figure 2). The iodine layers were found by the Patterson method, and the crystal structure was solved by direct methods in space group $P1$. A search for higher symmetry with the program MISSYM (Le Page, 1987) including the fluorine atoms of the CF_3 group indicated that there is no higher symmetry, but without them the program shows that there is higher symmetry.[25b] With the elements of symmetry found in MISSYM (4-fold rotatory inversion axis, 2-fold rotation axis, "diamond" glide plane) and the space group suggestions made in XPREP, the space group $I\bar{4}2d$ (No. 122) was found. The systematic absences (hhl) $2h + l = 4n + 1$ and ($0kl$) $k + l = 2n + 1$ conform to this space group and the structure was transformed from $P1$ to $I\bar{4}2d$ via the matrix (100, 010, 112). The layers of the fluorine atoms of the CF_3 group have occupation factors of 0.5, and the CF_3 group is rotating or disordered. The Flack X parameter shows values of nearly 0.19, and the absolute structure cannot be determined reliably. A final refinement with anisotropic thermal parameters gave values of R_1(all data) = 0.0341 and R(int) = 0.0746. For the data reduction, structure solution, and refinement, programs in the SHELXTL package and PARST were used.[26−28] The crystal data are summarized in Table 1.

The molecule has a distorted trigonal bipyramidal structure with the two fluorine atoms in the apical position and the trifluoromethyl group in the equatorial position. This is in accordance with the Gillespie−Nyholm theory and the structure can be described as T-shaped.[29,30] The same conformation is found in ClF_3 and BrF_3.[31,32] Bond lengths and selected angles of CF_3IF_2 are summarized in Table 2.

The I−F bond lengths are 1.982(2) Å, and the angle between the two apical fluorines is 165.4(2)°. Because no crystal structure of IF_3 is available, the I−F bond lengths are compared to those in IF_2^- (2.075−2.082 Å),[33] IF_4^- (2.000−2.018 Å),[33]

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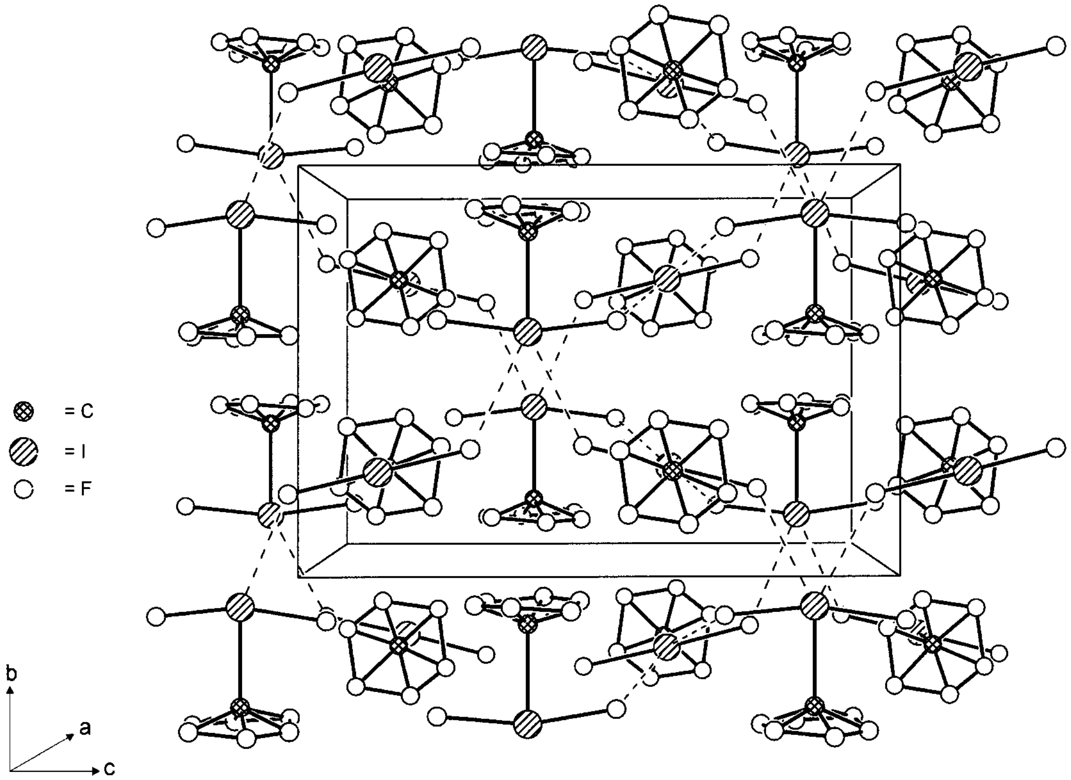

Figure 2. View of the unit cell and the molecules in its nearest environment. The molecules are connected in the form of zigzag chains by I−F contacts 2.95 Å long.

Table 1. X-ray Diffraction Data of CF_3IF_2

space group	$I\bar{4}2d$ (No. 122)
a, Å	8.5090(10)
b, Å	8.5090(10)
c, Å	12.324(2)
volume, Å^3	892.3(2)
ρ_{calcd}, g cm^{-3}	3.482
Z	8
fw, g mol^{-1}	233.91
μ, cm^{-1}	71.72
T, °C	−100(2)
λ, Å	0.710 69
R^a [$I > 2\sigma(I)$]	$R_1 = 0.0239$, $wR_2 = 0.0412$
R^a (all data)	$R_1 = 0.0341$, $wR_2 = 0.0426$

[a] $R = \sum||F_0| - |F_c||/\sum|F_o|$. Refinement method: full-matrix least-squares calculations based on F^2.

Table 2. Bond Lengths (Å) and Selected Angles (deg) for CF_3IF_2[a]

I(1)−F(1)	1.982(2)	F(1)−I(1)-F(1a)	165.4(2)
I(1)−F(1a)	1.982(2)	F(1)−I(1)-C(1)	82.71(9)
I(1)−C(1)	2.174(6)	F(1a)-I(1)−C(1)	82.71(9)
F(2)−C(1)	1.352(8)	F(2)−C(1)-I(1)	106.2(5)
F(3)−C(1)	1.286(8)	F(3)−C(1)-I(1)	110.7(6)
F(4)−C(1)	1.235(7)	F(4)−C(1)-I(1)	112.9(5)
		F(3)−C(1)-F(2)	105.9(6)
		F(4)−C(1)-F(2)	107.6(7)
		F(4)−C(1)-F(3)	113.0(6)

[a] Symmetry transformations used to generate equivalent atoms: a = $x, -\frac{1}{2} - y, \frac{1}{4} - z$.

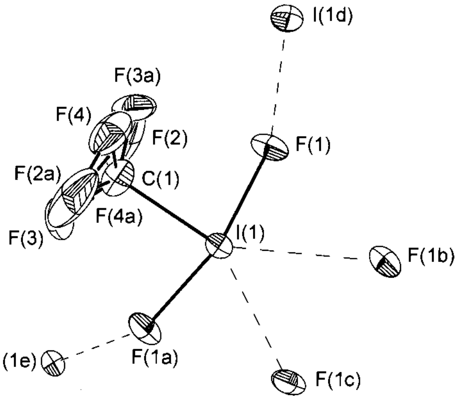

Figure 3. Projection of a CF_3IF_2 molecule with its contacts. The resulting coordination polyhedron is a distorted trigonal bipyramid. The angles built by these contacts are 63.76(8)° F(1b)−I(1)−F(1c) and 129.02(11)° I(1)−F(1a)−I(1e) or I(1)−F(1)−I(1d)]. Symmetry transformations are a = $x, -\frac{1}{2} - y, \frac{1}{4} - z$; b = $1 - y, -1 + x, -z$; c = $1 - y, \frac{1}{2} - x, \frac{1}{4} + z$; d = $1 + y, 1 - x, -z$; $e = \frac{1}{2} - y, -\frac{3}{2} + x, \frac{1}{2} - z$. Thermal ellipsoids are drawn at the 50% probability level.

IF_6^- (1.821−2.114 Å),[34] IF_5 (1.75 Å(ap), 1.87 Å(eq)), and CF_3IF_4 (1.904−1.925 Å).[35,12] As expected, the value for the I−F bond is in the range for a iodine(III) compound and, as the comparison between IF_5 and CF_3IF_4 shows, is slightly longer than those estimated for IF_3 (1.971 Å(ap), 1.901 Å(eq)).[36] This results from the higher space requirement of the CF_3 group in comparison with a fluorine ligand.

The angle between the two apical fluorines shows a large deviation from the ideal value of 180°. The explanations for this are the repulsion between and the high space requirement of the two lone pairs and the contacts made by the molecules. The same effect is observed for ClF_3 and BrF_3 with angles of 174 and 170.4°, respectively.[31,32] In case of CF_3IF_4, where the lone pair and the four intermolecular contacts press the four

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Table 3. Raman and IR Frequencies of CF_3IF_2 at Various Temperatures

Raman		IR		
−78 °C	−100 °C[a]	−70 °C	−250 °C[a]	assignment
51 m	52 (0.83)			$\nu_{15}\ \tau(A'')$
	67 (0.3)			lattice modes
80 m	82 (0.83)			lattice modes
213 w	213 (0.4)			$\nu_{10}\ \delta IF_2\ (A')$
248 w (sh)	250 (0.76)			$\nu_9\ \rho CF_3\ (A')$
263 w (sh)	265 (0.96)			$\nu_8\ \gamma IF_2\ (A')$
			280 w	
285 m	285 (3.0)	281 m		$\nu_7\ \nu CI\ (A')$
			288 sh	
324 vw		324 w		
			448 vs	
		457 m		
			466 sh	
	475 (0.3)			$\nu_{12}\ \delta CF_3\ (A'')$
		477 m	476 vs	$n_6\ \nu IF_2\ (A')$
			490 sh	
499 vs	500 (10)	506 sh		$\nu_5\ \nu IF_2\ (A')$
			525 w	
546 vw	545 (0.4)	553 m	548 w	$\nu_4\ \delta CF_3\ (A')$
		608 w		
		668 w		
692 vw				
			726 w	
	745 (0.3)	747 s	745 s	
756 m	760 (2.4)		754 sh	$\nu_3\ \delta CF_3\ (A')$
		1025 s (sh)	1026 m (sh)	
	1050 (0.2)	1056 vs	1054 vs	$\nu_2\ \nu CF_3\ (A')$
			1065 vs (sh)	
1108 m	1110 (0.83)			$\nu_1\ \nu CF_3\ (A')$
		1199 vs	1194 vs	$n_{11}\ \nu\ CF_3\ (A'')$
		1232 vs (sh)	1218 vs	
		1296 w	1295 vw	

[a] Reference 7.

equatorial fluorines out of the plane toward the CF_3 group, the resulting C−I−F angles are in the range of 83° instead of 90°.[12]

The unit cell contains eight formula units and each molecule has contacts to four adjacent molecules (Figure 3). Two contacts are made by the apical fluorines, and the others are made by the iodine. This is due to strong cross-links between the molecules to give zigzag chains. The lengths of all these contacts are 2.950 Å, and the sum of the van der Waals radii published by Bondi is 3.45 Å.[37] The angle of the asymmetrical fluorine bridge (I−F- - -I) is 129.02(11)°, and that of the symmetrical iodine bridge (F- - -I- - -F) is 63.76(8)°. These secondary bonds are not in the same direction as the lone pairs at the iodine, and the resulting coordination polyhedron is a distorted trigonal bipyramid. The contacts in CF_3IF_4 are comparable to those in CF_3IF_2 and show lengths of primary polar contacts to be 3.03 and 3.07 Å and secondary polar contacts to be 3.25 Å.[12]

Vibrational Spectra. The vibrational spectra of CF_3IF_2 have been described by Lehman, Naumann, and Stopschinski, and therefore we will discuss our results only briefly.[7]

The predicted C_s symmetry can be confirmed, but there is a deviation of nearly 8° between the mirror plane and the C−F bonds of the CF_3 group basically of the eclipsed conformation. In the spectra the resulting fifteen fundamental vibrations, except $\nu_{14}(\delta IF_2\ A'')$ and $\nu_{13}(\rho CF_3\ A'')$, were observed. The frequencies and assignments shown in Table 3 conform to those made by Naumann et al., with exception of $\nu_6(\nu IF_2)$, which is in the staggered conformation in the A″-mode caused by the symmetry.

In the Raman spectrum $\nu IF_2(A')$ is the strongest line at 499 cm^{-1}, and the deformations of this group occur in the range of 213−263 cm^{-1}. For the CF_3 group the deformations can be found between 546 and 756 cm^{-1}, the line at 248 cm^{-1} is assigned to the $\rho CF_3(A')$, and the stretching vibrations are between 1056 and 1232 cm^{-1}. The weak line at 1050 cm^{-1} observed by Naumann et al., which was assigned to $\nu CF_3(A')$, could not be detected.[7] The C−I stretching vibration is found at 285 cm^{-1} in the Raman spectrum. This assignment is in good agreement with that of CF_3I.[38]

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft.

Supporting Information Available: Listings of crystal data and intensity collection parameters, anisotropic thermal parameters, and all bond lengths and angles are available (4 pages). Ordering information is given on any current masthead page.

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