Graphical Abstract - Synopsis

1,4-diiodooctafluorobutane was found to react with potassium *tert*-butoxide in dioxane to afford a halogen-bonded adduct as a white precipitate. Single crystal X-ray analysis of the precipitate reveals an extended network held together by strong iodine-oxygen interactions. The oxygen-iodine bond length in the *tert*-butoxide complex was found to be 2.391(6) Å, much shorter than a previously published and similar complex involving dioxane (2.814(12) Å). To our knowledge, this work represents the first example of a structurally characterized halogen bonding network involving anionic oxygen donor atoms with perfluoroalkyl iodides. The *tert*-butoxide adduct displays the shortest iodine-oxygen distance and the longest iodine-carbon distance thus far reported for any halogen bonding involving perfluoroalkyl iodide substrate.

An Unusual Example of Halogen Bonding to Potassium *t*-Butoxide

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Table of Contents Graphic

Abstract: 1,4-diiodooctafluorobutane was found to react with potassium *tert*-butoxide in dioxane to afford a halogen-bonded adduct as a white precipitate. Single crystal X-ray analysis of the precipitate reveals an extended network held together by strong iodine-oxygen interactions. The oxygen-iodine bond length in the *tert*-butoxide complex was found to be 2.391(6) Å, much shorter than a previously published and similar complex involving dioxane (2.814(12) Å). To our knowledge, this work represents the first example of a structurally characterized halogen bonding network involving anionic oxygen donor atoms with perfluoroalkyl iodides. The *tert*-butoxide adduct displays the shortest iodine-oxygen distance and the longest iodine-carbon distance thus far reported for any halogen bonding involving a perfluoroalkyl iodide substrate.

Keywords: Fluoroalkylation; halogen bonding, fluorine

1. Introduction

The ability of halogen atoms in certain molecules to interact with electron donors has been exploited in such fields as crystal engineering, anion recognition, and self-assembly processes.[1-9] Halogen bonding may also be important for mechanistic considerations in synthetic reactions,[10] and as complements or alternatives to hydrogen bonding in the assembly of biological supermolecules.[11] According to IUPAC, “A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity.”[12]

Perfluoroalkyl iodides have served as an especially active halogen bonding partners, especially to nitrogen donor molecules.[13-17] X-ray analyses of these nitrogen supported halogen-bonded architectures indicate that the N $\cdots$ I bond length is typically around 2.80 Å in the solid state (or approximately 0.8 times the sum of the van der Waals radii for nitrogen and iodine).[16] Moreover, the angle formed by the covalent and the noncovalent bondings around the halogen were approximately linear (spanning from 177° to 165°), consistent with the n $\rightarrow$ σ^* character of the interaction.[18, 19] Furthermore, it was observed that in general, the stronger the halogen bonding, the greater the lengthening of the C-I bond, consistent with an electron donation from nitrogen to iodine.[20] Resnati and co-workers showed that when α,ω -perfluoroalkyl diiodides were used as a substrate, the donor-acceptor interactions involving nitrogen-iodine bonds are doubled, affording strongly bound self-assembled and infinite one-dimensional chains.[16] Indeed, upon reaction of perfluoroalkyl polyiodides with neutral bidentate nitrogen donor molecules, supramolecular architectures of various flavors could be obtained.[3, 16]

Figure 1. Infinite chains formed by oxygen-iodine interactions of **1** ($n = 1$) in the solid state.[17]

Oxygen is a weaker electron donor than nitrogen for halogen bonding,[17] and so thus far the majority of examples of halogen bonding to α,ω -perfluoroalkyl diiodides have been with nitrogen donors like amines and imines. Zhu and co-workers, however, showed crystallographically that oxygen donors like dioxane and hexamethylphosphoramide can form infinite chains with α,ω -perfluoroalkyl diiodides like that shown in Figure 1.[17] The distance between oxygen and iodine in **1** was measured to be 2.814(12) Å, which was shorter than the sum of the van der Waals radii of iodine (1.98 Å) and oxygen (1.52 Å). This example showed clearly the nature and the degree of the halogen bonding with neutral oxygen donors molecules. However, there have been no examples of halogen bonding of perfluoroalkyl iodides with *anionic* oxygen donor molecules that have been structurally characterized. Such an adduct would be interesting to analyze, as although amines with higher energy lone pairs form more stable adducts than do neutral oxygen donors, anionic oxygen donors may have the energy of its lone pair raised relative to amines leading to even stronger halogen bonded adducts. An infrared and NMR study has detected a halogen bonding interaction between CF_3I and $[\text{Me}_4\text{N}][\text{OCF}_3]$, but that species was stable only at low temperatures.[13] Herein, we describe in detail the strong and stable halogen bond that forms between 1,4-diiodooctafluorobutane and potassium *tert*-butoxide.

2. Results and Discussion

Upon mixing 1,4-diiodooctafluorobutane with potassium *tert*-butoxide in dioxane, the immediate precipitation of **2** as a white solid (eq 1) was observed. Solvent choice was critical as the use of acetonitrile instantly generated $\text{H}(\text{CF}_2)_4\text{H}$ and led to a black mixture at room temperature. The formation of $\text{H}(\text{CF}_2)_4\text{H}$ was also observed in THF, Et_2O and DMSO. The compound was stable in DMF and benzonitrile, however, and showed no signs of $\text{H}(\text{CF}_2)_4\text{H}$ formation in those solvents. NMR spectroscopy supported the formation of a halogen-bonded adduct. The ^{19}F NMR chemical shifts for the pure 1,4-diiodooctafluorobutane in DMF appear at $\delta = -61$ and -113 , whereas the halogen bonded complex **2** exhibited resonances far more upfield at $\delta = -88$ and -114 in DMF. A strong binding interaction with potassium *tert*-butoxide is not unique to the 1,4-diiodooctafluorobutane substrate. If the monoiodide species 1-iodo-perfluorobutane is used as the acceptor, an even larger $\Delta\delta = 26$ for the RCF_2I signals was observed. However, unlike 1,4-diiodooctafluorobutane, the potassium *tert*-butoxide complex with 1-iodo-perfluorobutane does not precipitate from dioxane, suggesting a supramolecular lattice similar to **2** is not formed. ^{19}F NMR chemical shift differences have previously been used to characterize the strength of the halogen bonding. It was established that RCF_2X signals show large high-field shifts upon halogen bonding formation, and the stronger the interaction, the larger the shift.[19] The $\Delta\delta = 21$ and 26 in DMF solvent for the CF_2I resonances that we observed for the *tert*-butoxide adducts are the largest differences thus far reported for halogen bonding interactions involving perfluoroalkyl iodides. For comparison, $\Delta\delta = 4.9$ was observed for the neutral dioxane adduct **1**. [17]

Since we were unaware of any examples of halogen bonding of perfluoroalkyl iodides to potassium *tert*-butoxide, an X-ray investigation of **2** was performed. The solid that precipitated from dioxane could be recrystallized from DMF/trifluorotoluene, and the X-ray analysis confirms the nature of the bonding in **2** (Figure 2). While the iodine-oxygen bond length in the dioxane complex **1** was measured to be $2.814(12) \text{ \AA}$, [17] the iodine-oxygen bond length in **2** was found to be much shorter at $2.391(6) \text{ \AA}$. This distance approaches the average iodine-oxygen *covalent* bond of $(2.14 \text{ \AA})$. [17, 21] The iodine-carbon

bond length in **2** is 2.281(8) Å, which to our knowledge is the largest elongation observed in halogen-bonded complexes to perfluoroalkyl iodides and is consistent with an electron donation from oxygen to iodine.

Figure 2. Solid-state structure depicting the networked arrangement of **2**. Color scheme: O red, C grey, F yellow-green, I magenta, K purple. The disordered potassium-bound DMF solvent molecules have been omitted for clarity. Selected bond lengths (Å): iodine-carbon 2.281(8); iodine-oxygen 2.391(6).

With regards to the supramolecular architecture that is produced, the X-ray analysis reveals that the use of anionic instead of neutral oxygen donors has introduced another dimensionality to the extended molecular network. The network is not an infinite chain, as has previously been observed with neutral oxygen donors, but rather infinite sheets by virtue of the fact that the potassium counter-ions can chelate to multiple iodine atoms. This data raises the intriguing possibility that the use of other counter-cations might lead to more complex architectures, including those possessing three-dimensionality.

3. Conclusions

We have shown that 1,4-diiodooctafluorobutane reacts with potassium *tert*-butoxide in dioxane to afford a halogen-bonded adduct with an extended two-dimensional network held together by strong iodine-oxygen interactions. The new complex represents the first example of a structurally characterized halogen bonding network involving anionic oxygen donor atoms with perfluoroalkyl iodides. The *tert*-butoxide adduct displays the shortest iodine-oxygen distance and the longest iodine-carbon distance thus far reported for any halogen bonding interactions involving perfluoroalkyl iodide substrate.

4.0 Experimental Procedures

4.1 General Considerations: All manipulations were performed under an inert atmosphere using standard Schlenk and high vacuum techniques or in a nitrogen filled glovebox.¹¹ Solvents were purified by passing through activated alumina and/or copper in a solvent purification system supplied by Pure Process Technology. 1,4-diiodooctafluorobutane was purchased from SynQuest Labs, Inc. and used without further purification. Solution ¹H NMR spectra were recorded at ambient temperature on a Bruker DRX 500 MHz spectrometer and referenced to residual proton solvent signals. ¹³C NMR spectra were recorded on a Bruker NMR spectrometer operating at 125 MHz and referenced to solvent signals. ¹⁹F spectra were recorded on the Bruker NMR spectrometer operating at 470 MHz and referenced to α,α,α -trifluorotoluene at δ -67.3. A Bruker D8 Quest diffractometer was used for X-ray crystal structure determinations.

4.1.1. Synthesis of complex 2: 450 mg (4 mmol) of potassium *t*-butoxide was dissolved in 4 mL of 1,4-dioxane. To this was added dropwise 453 mg (1 mmol) of 1,4-diiodooctafluorobutane in 4 mL of 1,4-dioxane. The mixture was stirred at room temperature for 15 min. Then the mixture was filtered through a glass frit and the residue was washed with diethyl ether. The residue was then dried under

vacuum to remove all the volatiles to yield 780 mg of an off-white powder (the amount of dioxane molecules coordinated to potassium at this stage is unknown). The off-white powder was then dissolved into a 1:5 mixture of DMF:trifluorotoluene and placed in a -35 °C freezer overnight to form colorless crystals suitable for X-ray analysis. ¹⁹F NMR (DMF-*d*₇, 470 MHz): δ -88 (br s), -114 (br s). The thermal and air-sensitivity of **2** precluded elemental analysis. Crystallographic data (excluding structure factors) for compound **2** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1050288. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

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