Fluorine-Containing Donor−Acceptor Complex: Infinite Chain Formed by Oxygen···Iodine Interaction

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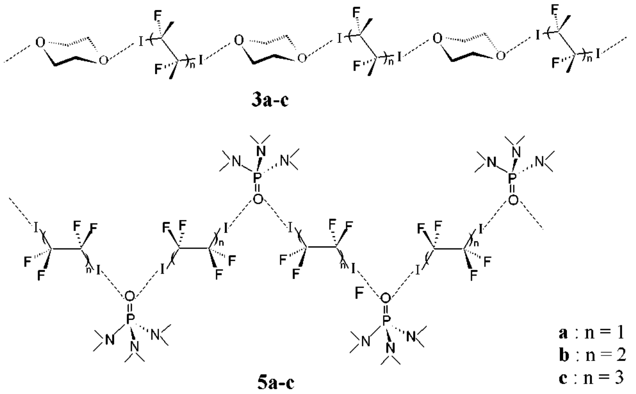
For many years, chemists have recognized that complexes may be obtained from stable compounds, formation of which is contrary to the normal rules of valency.[1−3] For the importance of the study of complexes to supramolecular chemistry, drug design, and biological systems, much work has been conducted in this field, which lies in the intermediate regime between bonding and nonbonding, to determine different aspects of intermolecular interaction.[4−10]

Per(poly)fluorocarbons have been drawing interest for their technological relevance,[11] and special physical and chemical properties.[12] In 1965, it was reported, on the basis of the phase-change diagram of the solution, that donor−acceptor complexes are formed between perfluoroalkyl iodides and amines.[13] Thereafter, a number of complexes and their X-ray structure of perfluoroalkyl iodides interacting with amines have been published.[14,15] Oxygen is a weaker electron donor in this kind of interaction than nitrogen.[15b] Few complexes of $O\cdots I{-}R_f$ (R_f = per(poly)fluoroalkyl) have been reported, and they gave a wrong complex structure.[14] In this contribution, we report two different kinds of the endless chains of alternating α,*ω*-diiodoperfluoroalkane and oxygen (Scheme 1).

Scheme 1



From an equimolar mixture of 1,2-diiodotetrafluoroethane **1a** and 1,4-dioxane **2** in chloroform, the complex **3a**[16] is isolated as colorless crystals. The structure of **3a** is shown in Figure 1. The endless chains of alternating 1,2-diiodotetra-fluoroethane and 1,4-dioxane depend on oxygen···iodine interactions running in a direction which approximately resembles the equatorial direction in cyclohexane. The distance between O and I is 2.814(12) Å which is considerably longer than the average covalent bond between O and I (2.14 Å),[17] but it is also definitively shorter than the sum of the corresponding van der Waals radii of O (1.52 Å)[18] and I (1.98 Å).[18] Moreover, the three atoms $O\cdots I{-}C$ are approximately linear 163.3(3)°. This interaction compares well with the interaction between 1,4-dioxane with I_2 or Br_2.[19]

Since *n* donor atoms such as oxygen possess two lone electron pairs, the question arises whether a particular donor atom may be involved in more than one electron donor−acceptor bond to

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(16) Compounds **3(a−c)** or **5(a−c)** have been obtained similarly. Their structures were fully characterized by element analyses and other spectroscopic data. The synthesis of compound **3a** is first issued (ref 14) with an incorrect structure and without spectroscopic data. Crystal data for **3a**: $ICF_2CF_2I{\cdot}O(CH_2CH_2)_2O$; fw 441.93; trigonal, space group *R*-3; $a = b = 8.924(1)$ Å, $c = 13.447(1)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$; $Z = 3$; $D_c = 2.374$ g/cm^3; $\mu = 5.113$ mm^{-1}; $F(000) = 606$; colorless prismatic crystals, 3242 reflections (489 unique) were collected on a Nonius Kappa-CCD with monochromated Mo Kα radiation (0.71073 Å) at 200 K. Crystal data for **5b**: $I(CF_2CF_2)_2I{\cdot}O{=}P(NMe_2)_3$; fw 633.04; orthorhombic, space group $Pca2_1$; $a = 20.312(4)$ Å, $b = 8.679(8)$ Å, $c = 12.045(4)$ Å, $\alpha = \beta = \gamma = 90°$; $Z = 4$; $D_c = 1.980$ g/cm^3; $\mu = 3.108$ mm^{-1}; $F(000) = 1200$; colorless prismatic crystals, 2164 reflections (1972 unique) were collected on a Rigaku AFC-7r with monochromated Mo Kα radiation (0.71073 Å) at room temperature. For both structures, data were corrected for an empirical absorption and decay. The structures were solved by direct method and refined by full-matrix least-squares on F^2, using SHELXL 97. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were located at calculated positions and refined in the rigid mode. For **3a**: final R1= 0.0438 ($I > 2\sigma(I)$), 0.0830 (all data), wR2 = 0.0819 ($I > 2\sigma(I)$), 0.1183 (all data); $S = 1.046$; extinction coefficient = 0.0086(15); largest peak and hole = 0.620 e Å^{-3} and −0.592 eÅ^{-3}. For **5b**: final R1= 0.0556 ($I > 2^s(I)$), 0.0852 (all data), wR2 = 0.1481($I > 2\sigma(I)$), 0.1721 (all data); $S = 1.042$; extinction coefficient = 0.0054(9); largest peak and hole = 0.753 e Å^{-3} and −1.116 e Å^{-3}. The X-ray data files of in CIF, FCF format have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC −144262 (**3a**).

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Table 1. ^{19}F Chemical Shift Differences of **3** in Different Solvents

entry	solvent	$ICF_2{}^{\alpha}CF_2I$	$ICF_2{}^{\alpha}CF_2{}^{\beta}CF_2CF_2I$	$ICF_2{}^{\alpha}CF_2{}^{\beta}CF_2{}^{\gamma}CF_2CF_2CF_2I$
1	$\Delta\delta CF_2$ in 1,4-dioxane[a]	4.9^{α}	5.6^{α}, 1.0^{β}	5.5^{α}, 0.8^{β}, 0.3^{γ}
2	$\Delta\delta CF_2$ in HMPA	9.9^{α}	11.8^{α}, 1.5^{β}	12.3^{α}, 1.5^{β}, 0.3^{γ}
3	$\Delta\delta CF_2$ in 1,3-dioxolane	4.8^{α}	5.2^{α}, 0.8^{β}	4.7^{α}, 0.5^{β}, 0.2^{γ}
4	$\Delta\delta CF_2$ in 2,2-dimethyl-1,3-dioxolane[b]	4.5^{α}	4.8^{α}, 1.2^{β}	4.9^{α}, 0.8^{β}, 0.3^{γ}
5	$\Delta\delta CF_2$ in trimethyl phosphate[b]	7.0^{α}	7.7^{α}, 0.7^{β}	8.0^{α}, 0.8^{β}, 0.1^{γ}
6	$\Delta\delta CF_2$ in triethyl phosphate	7.5^{α}	8.5^{α}, 1.2^{β}	9.2^{α}, 1.4^{β}, 0.4^{γ}
7	δCF_2 of pure compound **3**[c]	26.5^{α}	19.8^{α}, -34.7^{β}	19.4^{α}, -35.8^{β}, -43.6^{γ}

[a] $\Delta\delta CF_2 = \delta_{\text{pure sample}} - \delta_{\text{in solvent}}$. [b] We also obtain white solids from an equimolar mixture of **3a** and 2,2-dimethyl-1,3-dioxolane or trimethyl phosphate at −20 °C, but they are liquid at room temperature. Further research is in progress. [c] We used TFA as external standard in ^{19}F NMR with upfield negative ($\delta_{CFCl3} = \delta_{TFA} + 76.8$ ppm).

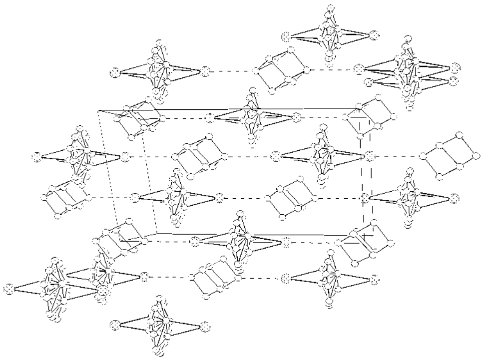

Figure 1. Crystal packing of **3a** viewed down the *a* axis. Two kinds of molecules were distinctly joined by O···I−C interactions (dotted lines). The disorder of both species was modeled using rigid body restraints.

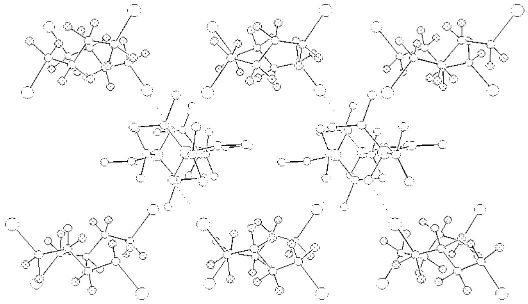

Figure 2. Crystal packing of **5b** viewed down the *c* axis. Two kinds of molecules were distinctly joined by O···I−C interaction (dotted lines).

halogen. This kind of complex is rarely reported in the literature.[20] In the crystal structure of **5b**[16] (Figure 2) the 1:1 complex of α,*ω*-diiodoperfluorobutane **1b** and hexamethylphosphoramide (HMPA) **4**, it was really found that each sp^2 oxygen interacts with two neighboring iodine atoms symmetrically. One by one, each α,*ω*-diiodoperfluoroalkane molecule is linked by two "oxygen bridges" to form the infinite chains. The P, O, and two I that interact with the same O atom are nearly in a plane. The three atoms, O···I−C, are approximately linear 177.0(8)° or 170.6(9)°, and the O···I distances are only 2.864(11) Å, 2.835(11) Å in **5b**, respectively, a little longer than sp^3 O···I distance in **3a**.

The compound **3a** is very volatile and easy to sublime ($\tau = 3$ min at 20 °C, 1.01×10^5 Pa). Thus, the X-ray diffraction analysis of this compound was carried out at 200 K. From the structure (Figure 1), the C atoms in **1a** are disordered along the *c* axis that joins the two iodine atoms, while the two C atoms in **2** are in three possible positions in the complex. In contrast, **5(a−c)** are more stable, and they can be stored at room temperature for several months without decomposition. However, when we collect the X-ray data of **5b** at room temperature, we also found considerable decay.

Apart from crystallographic methods, a principal technique for studying intermolecular interactions is spectroscopic analysis. ^{19}F NMR measurements rather than ^{1}H measurements can be applied in such donor−acceptor systems. Not only are the association constants of fluorine-containing acceptors with electron donors large compared with the corresponding complexes of the nonfluorinated acceptors, but also the Δ_0 values for ^{19}F are often at least double the values for ^{1}H[2]. From Table 1, we can find that the chemical shifts of CF_2 observed in ^{19}F resonances of **3** in solvents are apparently shifted upfield compared with that given in pure **3**. This change of the chemical shift is dramatically reduced with the increasing distance from the interactive O···I bond. The shift is essentially unchanged for the third CF_2 group. Obviously, the electron donation effect of solvents on the I atom exerts a major effect in the upfield shift of **3** in ^{19}F NMR spectra.

In summary, we present two different kinds of strong interactions between α,*ω*-diiodoperfluoroalkane and oxygen that pack in an analogous fashion. Meanwhile, a useful electron donor, hexamethylphosphoramide (HMPA), which is involved in two electron donor−acceptor bonds to halogen, is first reported.[21] Our research may offer an alternative for researchers who concentrate their study on charge-transfer interactions,[1b,3,5−7] molecular recognition,[22] reaction mechanism discussion,[12d,23] supramolecular[24] and many other prospective fields.[8,21,25]

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Supporting Information Available: Tables of crystallographic data, extensive figures of **3a** and **5b** (PDF). An X-ray crystallographic file, in CIF format, for **3a** and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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