Crystal Structure of a Supramolecular Complex Formed between 1-bromo-2-iodo-tetrafluoroethane and N,N,N′,N′-tetramethyl-ethylenediamine

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Abstract

X-ray analysis has revealed that N,N,N′,N′-tetramethyl-ethylenediamine **1** form donor–acceptor complex **3** with 1-bromo-2-iodo-tetrafluoroethane **2**, in which the N X (X = Br, I) distances are longer than the average covalent bond length between X and N, but are also definitively shorter than the sum of the corresponding van der Waals radii of X and N, thus that indicating weak interactions between the nitrogen and bromine or iodine atoms. In our experimental section, a valuable method for recrystallization and collect X-ray data from crystals that easily exhibit decay and can be cracked is reported.

Introduction

The charge-transfer interactions ($n \rightarrow \sigma^*$) between the electronegative atoms (N, O, S) and halogen atoms (I, Br, Cl) are strong, directional, and selective [1]. This type of interaction is very similar as hydrogen bond, so has been called halogen-bonding [2–8]. Recently, a number of X-ray structures of complexes of perfluoroalkyl iodides interacting with amines have been reported [9–12]. Theoretically, perfuoroalkyl bromides also can form donor–acceptor complexes with amines, though the bond Br $\cdots$ N is weaker than I $\cdots$ N. Some X-ray crystal structures of complexes of the latter type have been reported [13–16].

In this contribution, we now report one complex of this type. The complex is formed by equimolar mixture of 1-bromo-2-iodo-tetrafluoroethane, and N,N,N′,N′-tetramethyl-ethylenediamine (Scheme 1). The two type of compounds connect each other by Br $\cdots$ N and I $\cdots$ N interactions, so as infinite chains are formed.

Experimental section

Co-crystallization

The N,N,N′,N′-tetramethyl-ethylenediamine and 1-bromo-2-iodo-tetrafluoroethane were mixed in chloroform in equal molar ratio and the solvent was evaporated slowly. The crystals were then collected for recrystalli-zation. The melting point of the complex was measured on a Mel-Temp apparatus and is uncorrected (Table 1).

Recrystallization

Because of low quality of this type of crystal, all crystals have been recrystallized by sublimation method. The crystals were kept in a sealed glass tube at −20 °C for 2 months (60 days), then a crystal with suitable size from the inside wall of this tube was selected to be used for X-ray data collection.

X-ray crystal structure of 3

Most of this type of crystals easily sublime, and many reported structures shows disordered. Therefore, we have to collect data at low temperature, but this type of crystals may be cracked when the temperature decreasing. We decreased the temperature step by step, from 253 to 180 K, 1 °C/min. Single crystal X-ray data was collected from this complex on a NONIUS Kappa-CCD diffractometer at 180 K, with graphite mono-chromatized MoK$_\alpha$ radiation (λ = 0.71073 Å). Almost no decay has been observed. Absorption correction was based on Multi-Scan method [17, 18]. The structure was solved by application of direct method and was refined by full-matrix least-squares techniques using on F^2 in SHELXL-97 [19]. Details of data collection and refine-ment procedures were reported in Table 1, atomic coordinates and selected geometric parameters for **3** were listed in Table 2.

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Table 1. Crystallographic data for 3

	3
Empirical formula	$C_8H_{16}BrF_4IN_2$
Formula weight	423.04
Color/habit	Colorless/block
Melt point (K)	335–337
Program for data collection	Nonius Kappa CCD
Wavelength (Å)	0.71073
Data collection temperature (K)	180
Crystal system	Triclinic,
Space Group	$P\bar{1}$
Cell dimensions a (Å)	6.1449 (4)
b (Å)	6.7680 (4)
c (Å)	9.3682 (5)
α (°)	110.890 (3)
β (°)	97.478 (4)
γ (°)	95.024 (3)
Volume (Å^3)	357.11 (4)
Z	1
Calculated density (mg/m^3)	1.967
Absorption coefficient (mm^{-1})	5.062
F (000)	202
Crystal size (mm)	$0.40 \times 0.30 \times 0.15$
Θ range for data collection (°)	3.77–27.48
Limiting indices	$-7 \leq h \leq 7, -8 \leq k \leq 8, -12 \leq l \leq 12$
Reflections collected/unique	6672/1629
Completeness (%)/to Θ (°)	99.8/27.48
R (int)	0.0566
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1629/1/76
Goodness-of-fit on F^2	1.049
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0419$, w$R2 = 0.1033/1381$
R indices (all data)	$R_1 = 0.0511$, w$R2 = 0.1100/1629$
Extinction coefficient	0.048(6)
Largest diff. peak and hole (e/Å^3)	1.190 and −0.867

Results and discussion

E-statistics indicates centric symmetry for the triclinic crystal. However, we also solved the structure with non-centric symmetry (in P 1). This latter calculation yielded two I atoms and two Br atoms, the two atoms in calculation pair occupying centric symmetry-related positions. This result shows that in the infinite chain, every molecule of 1-bromo-2-iodo-tetrafluoroethane, randomly choices its direction, so the structure is not well orderered. The Br or I atoms have equal occupancy, 0.5, and the molecule has a symmetry center on the midpoint between two C_f atoms (See Figures 1 and 2).

The Br N distance is 2.863(5) Å. This distance is considerably longer than the average covalent bond length between Br and N (2.14 ± 0.02 Å) [20], but

Table 2. Atomic coordinates ($\times 10^4$), occupancy and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for non-hydrogen atoms of 3

Atom	x	y	z	Occupancy	Ueq
I	2820(4)	7701(4)	6441(2)	0.5	42(1)
Br	2949(6)	7413(6)	6793(3)	0.5	45(1)
C(1)	4348(16)	5543(16)	4646(11)	1.0	121(4)
F(1)	2769(6)	4313(7)	3507(4)	1.0	83(1)
F(2)	5716(9)	6801(6)	4173(6)	1.0	101(2)
C(2)	2896(10)	12556(10)	9343(6)	1.0	56(1)
C(3)	−321(11)	11679(10)	7386(7)	1.0	56(1)
N	953(6)	10988(6)	8503(4)	1.0	38(1)
C(4)	−506(7)	10611(7)	9535(5)	1.0	39(1)

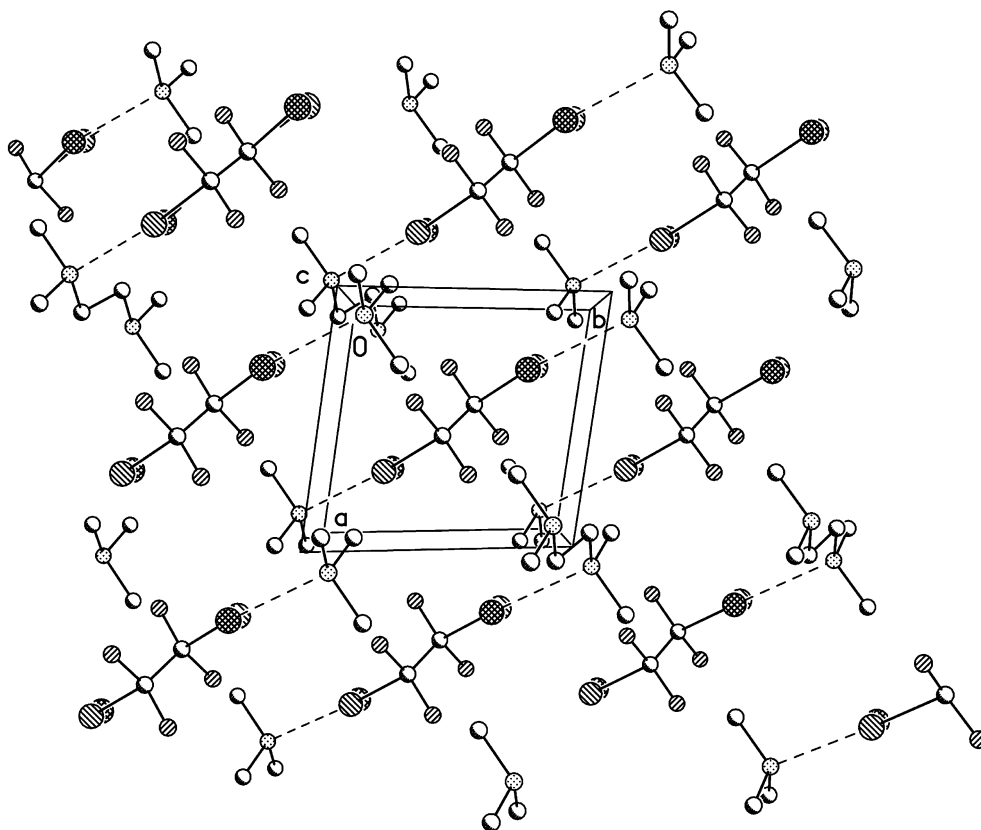Ueq is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Figure 1. Crystal packing of **3** viewed down the *c* axis. Two kinds of molecules were distinctly joined by N $\cdots$I–C and N $\cdots$Br–C interactions (dotted lines).

much shorter than the sum of the van der Waals radii of Br (1.85 Å) and N (1.55 Å) [21]. The distance between I and N (2.821(5) Å) is also much shorter than the sum of the van der Waals radii of I (1.98 Å) [18] and N

(1.55 Å). The angles of C–I N is 170.1(2)° and the angles of C–Br $\cdots$N is 150.7(2)°.

In summary, we presented one crystal structure which contains weaker R_f–Br $\cdots$N halogen bonding.
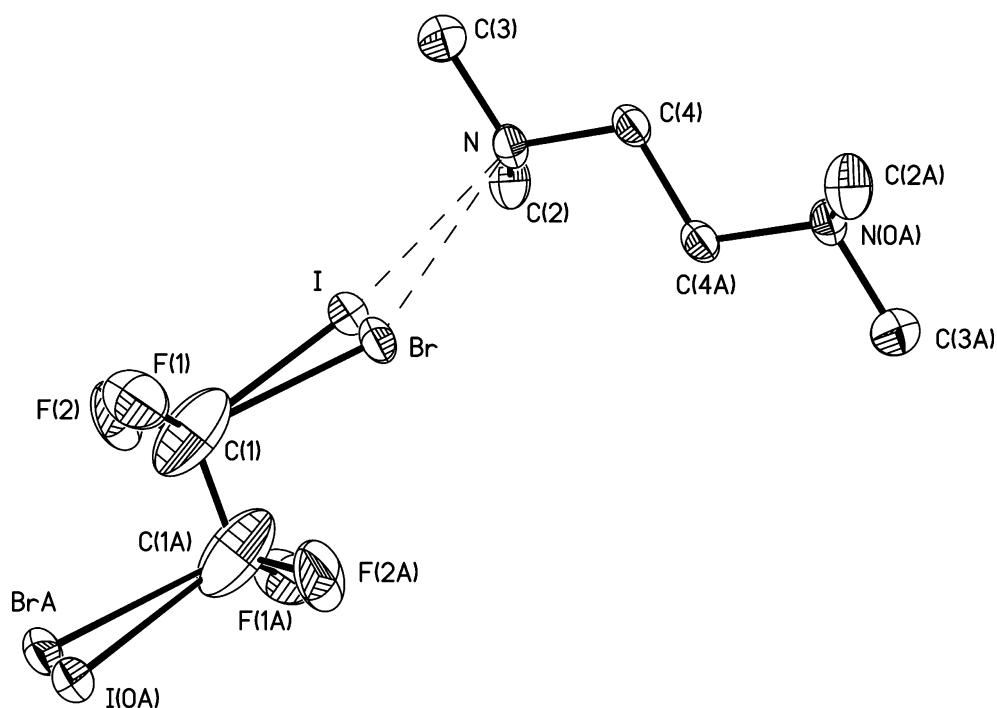

Figure 2. ORTEP plot of **3** with displacement ellipsoids drawn at 30% probability level. The hydrogen atoms are omitted.

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Halogen bonding is similar to hydrogen bond and can also be used in many researches in different fields. Both strong and weak halogen bonding will play important role on chemistry in many cases. Our research may offer a reference other researchers.

Crystallographic data in CIF format for the structure 3 have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC-186864. Copies of the data can be obtained, free of charge on application to CCDC, 12, union Road, Cambridge CB1 1EZ, UK (fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.au.uk).

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