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Communication

Co-existing Intermolecular Halogen Bonding and Hydrogen Bonding in the Compound *Trans*-5,10-bis(1-bromodifluoro-acetyl-1-ethoxycarbonyl-methylidene)thianthrene†

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Trans-5,10-bis(1-bromodifluoroacetyl-1-ethoxycarbonyl-methylidene)thianthrene (**1b**) was prepared from the reaction of $BrCF_2COC(N_2)CO_2Et$ with thianthrene. X-ray single crystal diffraction analysis showed that the intermolecular halogen bonding and hydrogen bonding coexisted in this compound. The bromine atom acted as an electron acceptor in the halogen bond and an electron donor in the hydrogen bond. It is the first example that the bromine atom acted as such a dual role in the hydrogen and halogen bond.

Keywords halogen bond, hydrogen bond, sulfur ylide, X-ray diffraction study

The hydrogen bonding interaction is most frequently used to assemble organic molecules in solid, liquid or gas phase, and plays an important role in stabilizing supramolecular aggregates.[1] The halogen bonding, which has received increasing attention recently, is the attractive interaction occurring between atoms possessing a lone-pair electron which acts as electron donor species, *i.e.* Lewis base, and halogen atoms which acts as electron acceptor species, *i.e.* Lewis acids.[2-7]

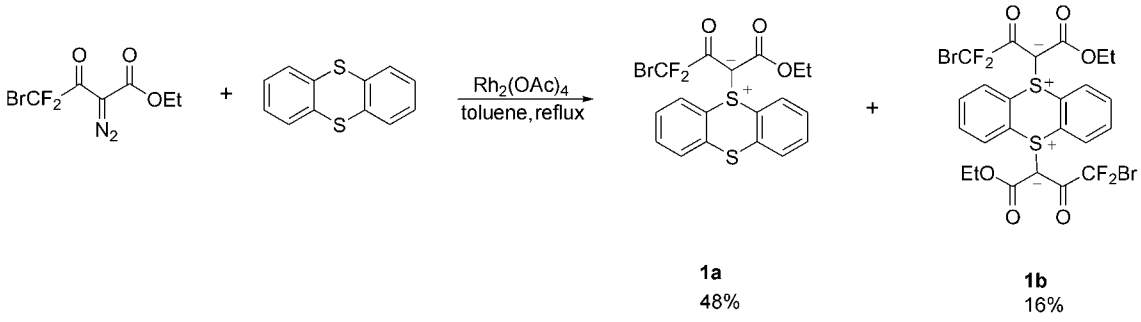
We have reported that oxygen-iodine interaction gave complexes with endless chains from α,ω-diiodoperfluoroalkanes $I(CF_2CF_2)_nI$ with 1,4-dioxane and HMPA.[8] Recently we presented a new class of supramolecular architecture of 1,1,3,3-tetra-oxo-2-bromo-4,4,5,5,6,6-hexafluoro-1,3-dithiacyclohexane and 2-methylpyrazine, which was assembled through co-existing hydrogen bonding and halogen bonding.[9] In this communication, we show the first example that co-existing intermolecular hydrogen bonding and halogen bonding share one same bromine atom in compound **1b**.

Compound **1b** was prepared from the reaction of $BrCF_2COC(N_2)CO_2Et$ with thianthrene in refluxing toluene in 16% yield (Scheme 1).

The sulfonium ylide has high melting point (198—200 ℃) and high stability. It remains unchanged after being refluxed in toluene for 24 h in the air. The high stability may be attributed to the two adjacent electron-withdrawing groups.

To establish the exact structure of **1b** and to explore why it is so stable compared to the corresponding non-fluoro-containing sulfonium ylide, this new compound was further analyzed by single X-ray crystal diffraction analysis. The molecular structure of **1b** and its packing diagram are showed in Figure 1.

Scheme 1



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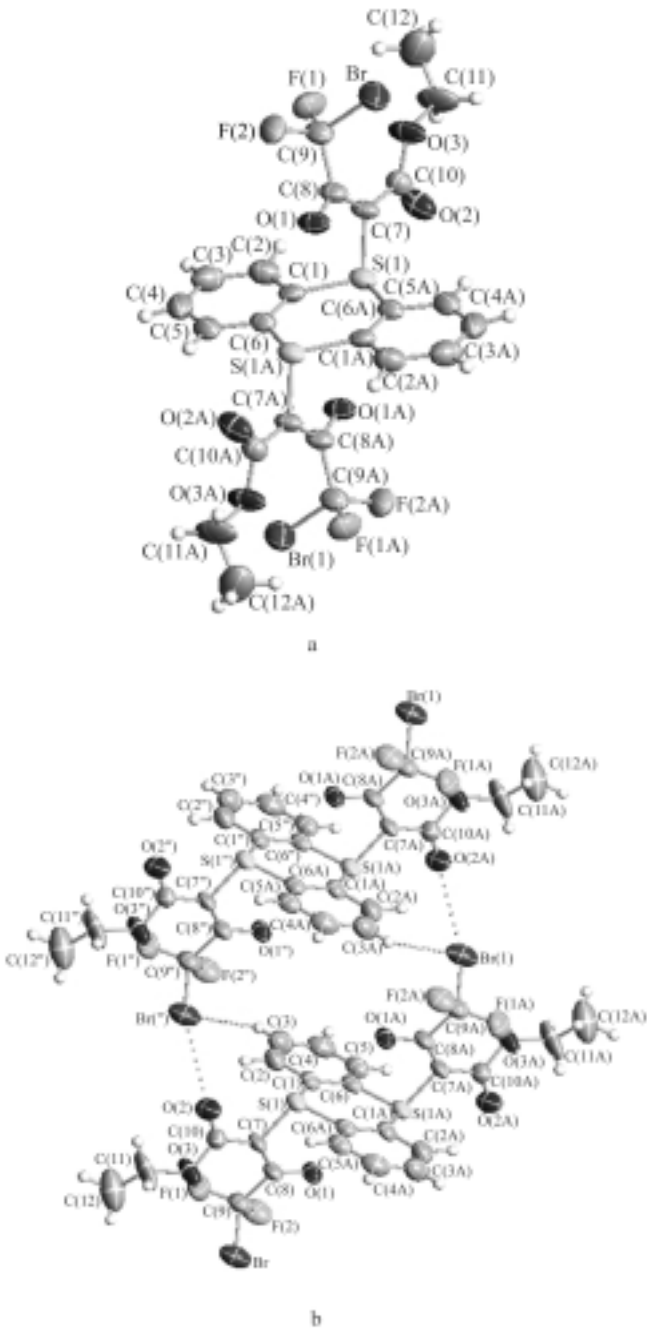

Figure 1 a: Molecular structure of compound **1b.** b: Packing diagram of compound **1b**.

Some crystal structure data of compound **1b** are listed in Table 1.

It was shown that the S(1)—C(7) bond length is 0.175 nm, which is close to the distance of C—S single bond. From Figure 1a it is clear that the two methylide groups, C(7)=S(1) and C(7A)=S(1A), were not co-planar with the thianthrene plane, and the dihedral angle between the plane containing C(7), C(8) and C(10) atoms and the thianthrene plane is 86°, so they are nearly perpendicular to each other. These results ruled out the fully conjugated planar structure **1b″** (see Figure 2). The bond lengths of C(7)—C(8) and C(7)—C(10) involving the methylide carbon are 0.145 nm and 0.142 nm, respectively, which is shorter than that of C—C

Table 1 Selected bond lengths (nm) and angle (°) for compound **1b**

Bond length/nm			
C(8)—O(1)	0.122	C(8)—C(7)	0.142
C(7)—C(10)	0.145	O(2)—C(10)	0.120
C(7)—S(1)	0.175	Br″···O(2)	0.314 (halogen bond)
Br″···H(3)	0.302 (hydrogen bond)		
Angle/(°)			
C(8)-C(7)-S(1)	113.89	C(10)-C(7)-S(1)	111.23
C(8)-C(7)-C(10)	134.88	C(9″)-Br″-O(2)	153.4
Br″-H(3)-C(3)	135.7	Torsion angle: S(1)-C(7)-C(8)-O(1) plane	11.17
Torsion angle: S(1)-C(7)-C(10)-O(2)	7.02	C(8)-C(7)-C(10)/ plane thianthrene	86

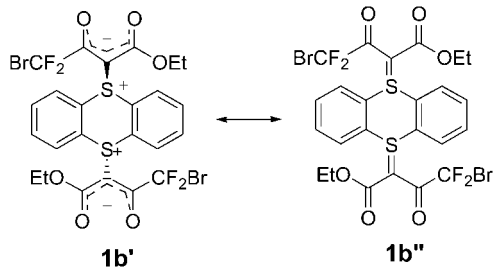

Figure 2 Two speculated possible structure conformations of **1b**.

single bond and longer than that of C=C double bond. And the bond lengths of two carbonyl C(8)=O(1) and C(10)=O(2) groups are 0.122 and 0.120 nm respectively. Therefore the structure conformation of **1b** should be depicted as **1b′**. The two adjacent carbonyl groups, especially the strong electron-withdrawing group bromodifluoroacetyl, can efficiently stabilize the ylide moiety.

It should be noticed that the intermolecular halogen bonding[10] C(9″)—Br″···O(2) and hydrogen bonding[11] C(9″)—Br″···H-C(3) co-exist in this compound as shown in Figure 1(b). The distance of Br″···O(2) is 0.314 nm, which is less than the sum of van der Waals radii (0.185 nm for Br and 0.152 nm for O). The C(9″)—Br″—O(2) is almost linear (153.4°). Thus, the oxygen atoms meet bromine atoms roughly in line with the C—Br bond, which is consistent with an n→σ* electron donation from oxygen to bromine.[9] In a known example,[11] the distance and the angle of the intermolecular halogen bond C—Br···O are 0.314 nm and 151.5°) in the crystal of 1,1,3,3-tetra-oxo-2-bromo-4,4,5,5,6,6-hexafluoro-1,3-dithiacyclohexane. The structure of **1b** did not suit what we earlier speculated, and it could form the intramolecular halogen bond, leading to a more favorable six-membered ring (Figure 3).

The distance of Br″···H—C(3) is 0.302 nm, and the angle of Br″—H—C(3) is 135.7°. The bromine atom

here acted as not only the halogen bonding donor, but also the hydrogen bonding acceptor. To the best of our knowledge, it is the first example that the bromine atom acted as such a dual role in the hydrogen bond and halogen bond.

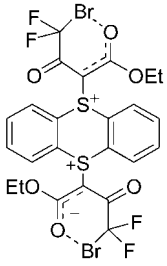

Figure 3 Probably existing intramolecular halogen bond.

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