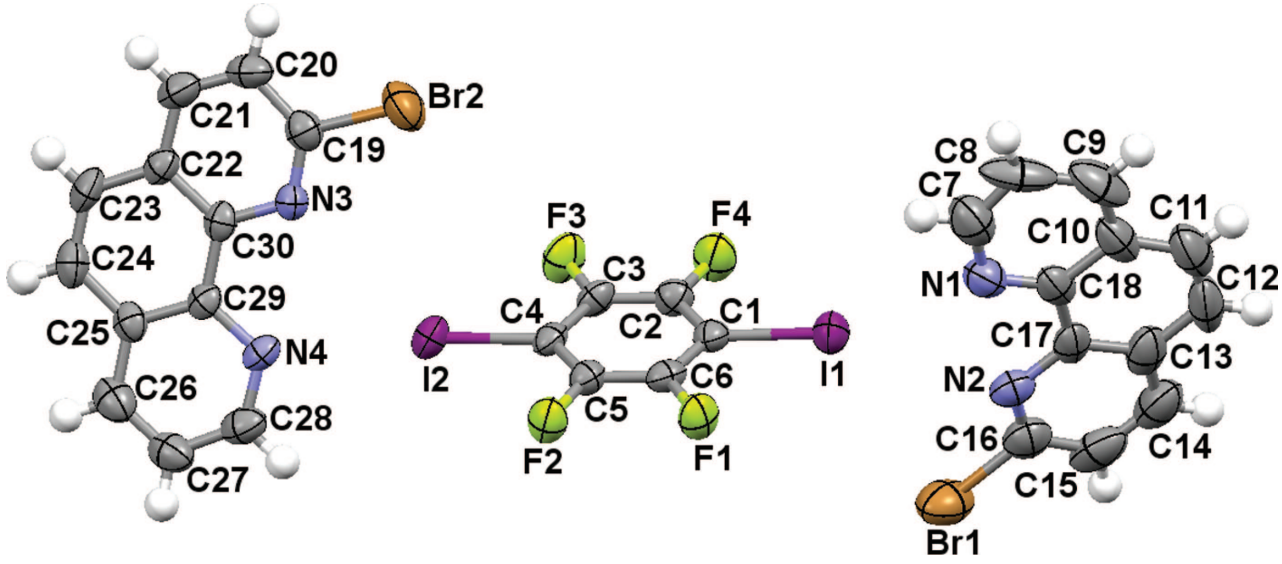
Limin Dang*, Saijin Huang and Aiwu Yin

Halogen bonds in the crystal structure of 2-bromo-1,10-phenanthroline – 1,4-diiodotetrafluorobenzene (2/1), $C_{30}H_{14}Br_2F_4I_2N_4$



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Abstract

$C_{30}H_{14}Br_2F_4I_2N_4$, monoclinic, $P2_1/c$ (no. 14), $a = 9.4531(3)$ Å, $b = 40.9487(15)$ Å, $c = 7.5118(3)$ Å, $\beta = 95.110(3)°$, $V = 2896.20(18)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0410$, $wR_{ref}(F^2) = 0.0828$, $T = 287.15(10)$ K.

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The asmmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.29 × 0.19 × 0.17 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	4.99 mm^{-1}
Diffractometer, scan mode:	SuperNova, EosS2, ω
θ_{max}, completeness:	25.5°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	15702, 5302, 0.034
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4198
$N(param)_{refined}$:	379
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], Olex2 [4]

Source of material

The 2-bromo-1,10-phenanthroline and 1,4-diiodotetrafluorobenzene for crystallization were purchased from J&K Scientific Ltd., and used without further purification. The halogen bond donor 1,4-diiodotetrafluorobenzene (4.02 mg, 0.01 mmol) and the halogen bond acceptor 2-bromo-1,10-phenanthroline (1.87 mg, 0.01 mmol) were dissolved in approximately 10 mL of trichloromethane with gentle stirring at room temperature. The undissolved materials were removed by filtration. The filtrate was set aside for crystallization by slow evaporation of the solvent at room temperature

***Corresponding author: Limin Dang,** School of Chemistry and Chemical Engineering, Hunan Institute of Engineering, Xiangtan 411104, China, e-mail: 13055155812@163.com
Saijin Huang and Aiwu Yin: School of Chemistry and Chemical Engineering, Hunan Institute of Engineering, Xiangtan 411104, China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
I1	0.68105(4)	0.43186(2)	0.75733(5)	0.05599(13)
I2	0.21943(4)	0.29892(2)	0.60234(5)	0.05202(12)
F1	0.5557(3)	0.37948(8)	1.0207(4)	0.0610(8)
F2	0.3856(3)	0.32868(8)	0.9625(4)	0.0601(8)
F3	0.3510(3)	0.35081(9)	0.3439(4)	0.0681(9)
F4	0.5264(4)	0.40052(9)	0.4022(4)	0.0735(10)
C1	0.5457(5)	0.39169(12)	0.7121(7)	0.0425(12)
C2	0.4915(5)	0.38297(13)	0.5439(7)	0.0474(13)
C3	0.4013(5)	0.35709(13)	0.5138(7)	0.0456(13)
C4	0.3621(5)	0.33783(12)	0.6509(7)	0.0415(12)
C5	0.4157(5)	0.34644(12)	0.8195(7)	0.0415(12)
C6	0.5054(5)	0.37284(13)	0.8506(7)	0.0429(12)
Br1	1.12347(8)	0.40803(2)	0.69455(11)	0.0957(3)
N1	0.7727(6)	0.50036(12)	0.8173(6)	0.0614(13)
N2	1.0118(5)	0.46839(12)	0.7419(6)	0.0567(12)
C7	0.6508(9)	0.51705(18)	0.8547(9)	0.082(2)
H7	0.5722	0.5040	0.8705	0.098*
C8	0.6317(10)	0.5472(2)	0.8703(8)	0.097(3)
H8	0.5455	0.5561	0.8964	0.116*
C9	0.7597(11)	0.56746(18)	0.8433(10)	0.094(3)
H9	0.7547	0.5901	0.8516	0.112*
C10	0.8859(8)	0.55266(15)	0.8059(8)	0.0696(18)
C11	1.0091(10)	0.57020(18)	0.7811(10)	0.089(2)
H11	1.0097	0.5927	0.7962	0.107*
C12	1.1289(10)	0.5548(2)	0.7351(9)	0.092(3)
H12	1.2089	0.5672	0.7167	0.110*
C13	1.1339(8)	0.52011(19)	0.7147(8)	0.075(2)
C14	1.2515(8)	0.5037(2)	0.6672(10)	0.089(2)
H14	1.3320	0.5153	0.6417	0.107*
C15	1.2498(7)	0.4701(2)	0.6574(9)	0.088(2)
H15	1.3277	0.4583	0.6248	0.105*
C16	1.1247(7)	0.45442(17)	0.6992(8)	0.0710(18)
C17	1.0125(6)	0.50187(15)	0.7503(7)	0.0563(15)
C18	0.8852(7)	0.51821(14)	0.7934(7)	0.0559(15)
Br2	−0.13553(8)	0.35698(2)	0.44785(10)	0.0778(2)
N3	−0.1211(4)	0.29064(10)	0.4288(5)	0.0412(10)
N4	0.0470(4)	0.23843(11)	0.5365(5)	0.0438(10)
C19	−0.2031(6)	0.31478(14)	0.3796(7)	0.0500(13)
C20	−0.3381(6)	0.31195(16)	0.2859(7)	0.0570(15)
H20	−0.3920	0.3303	0.2522	0.068*
C21	−0.3858(6)	0.28189(16)	0.2472(7)	0.0562(15)
H21	−0.4753	0.2791	0.1870	0.067*
C22	−0.3033(5)	0.25463(13)	0.2957(7)	0.0435(12)
C23	−0.3495(5)	0.22211(15)	0.2589(7)	0.0528(14)
H23	−0.4379	0.2185	0.1976	0.063*
C24	−0.2674(6)	0.19666(14)	0.3111(7)	0.0536(15)
H24	−0.2992	0.1756	0.2828	0.064*
C25	−0.1312(5)	0.20100(13)	0.4101(7)	0.0434(13)
C26	−0.0476(6)	0.17466(15)	0.4734(8)	0.0616(16)
H26	−0.0782	0.1534	0.4505	0.074*
C27	0.0786(6)	0.18037(15)	0.5686(8)	0.0612(16)
H27	0.1347	0.1632	0.6153	0.073*
C28	0.1217(6)	0.21268(15)	0.5944(7)	0.0578(15)
H28	0.2096	0.2164	0.6571	0.069*
C29	−0.0805(5)	0.23266(12)	0.4459(6)	0.0380(12)
C30	−0.1688(5)	0.26007(12)	0.3891(6)	0.0396(12)

conditions. After about two days, clear colourless crystals of title compound were obtained.

Experimental details

H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C).

Comment

In recent years, the studies of the non-covalent bonds such as the halogen bond and chalcogen bond are hot areas of research [5, 6]. It has been demonstrated that these new types of non-covalent bonds can be used in quite different fields spanning from crystal engineering to biomolecular recognition and drug design [5–8]. Wang and coworker reported the crystal structure of the cocrystal formed between 2-chloro-1,10-phenanthroline and 1,4-diiodotetrafluorobenzene [9]. In the present study, we reported the crystal structure of the cocrystal formed between 2-bromo-1,10-phenanthroline and 1,4-diiodotetrafluorobenzene.

All bond lengths and angles in the title crystal structure are in the normal ranges. One 1,4-diiodotetrafluorobenzene molecule and two 2-bromo-1,10-phenanthroline molecules are linked by two asymmetrical bifurcated halogen bonds with d(I1···N1) = 2.958 Å, <(C1-I1···N1) = 159.45°, d(I1···N2) = 3.477 Å, <(C1-I1···N2) = 150.59°, d(I2···N3) = 3.381 Å, <(C4-I2···N3) = 135.92°, d(I2···N4) = 2.981 Å and <(C4-I2···N4) = 173.16° to form the asymmetrical unit. The asymmetrical units are linked through π···π stacking interactions between two 2-bromo-1,10-phenanthroline molecules to form the 3D structure. According to the quantum chemical calculations, the π···π stacking interaction between two 1,4-diiodotetrafluorobenzene molecules is much weaker than the halogen bond with the type of C-I···N [10, 11]. As expected, no π···π stacking interactions between two 1,4-diiodotetrafluorobenzene molecules are found in the crystal structure of the title complex.

It is significant to compare the crystal structure of the cocrystal formed between 2-chloro-1,10-phenanthroline and 1,4-diiodotetrafluorobenzene with the crystal structure of the cocrystal formed between 2-bromo-1,10-phenanthroline and 1,4-diiodotetrafluorobenzene. The crystal structures of the two cocrystals are obviously different. Crystallization of 2-chloro-1,10-phenanthroline and 1,4-diiodotetrafluorobenzene yields cocrystal in monoclinic space group $I2/a$, whereas crystallization of 2-bromo-1,10-phenanthroline and 1,4-diiodotetrafluorobenzene yields cocrystal in monoclinic space group $P2_1/c$. Different from the case in the crystal structure of the cocrystal formed between 2-bromo-1,10-phenanthroline and 1,4-diiodotetrafluorobenzene, we found the π···π stacking

interactions between the 1,4-diiodotetrafluorobenzene molecule and the 2-chloro-1,10-phenanthroline in the crystal structure of the cocrystal formed between 2-chloro-1,10-phenanthroline and 1,4-diiodotetrafluorobenzene. All these results indicate the crystal structures can be tuned by changing the substituents of the compounds used.

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