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Halogen bonds in the crystal structure of 4,3:5,4-terpyridine – 1,4-diiodotetrafluorobenzene (1/1), $C_{21}H_{11}F_4I_2N_3$

Figure 1: Molecular structure of the title complex with displacement ellipsoids drawn at the 50% probability level.

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Abstract

$C_{21}H_{11}F_4I_2N_3$, monoclinic, $C2/c$ (no. 15), $a = 17.9705(8)$ Å, $b = 6.5423(3)$ Å, $c = 17.8916(8)$ Å, $\beta = 98.634(4)^\circ$, $Z = 4$, $V = 2079.65(16)$ Å³, $R_{\text{gt}}(F) = 0.0313$, $wR_{\text{ref}}(F^2) = 0.0784$, $T = 290$ K.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.24 \times 0.18 \times 0.14$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	3.07 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max} , completeness:	29.3° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	8418, 2486, 0.026
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2044
$N(\text{param})_{\text{refined}}$:	137
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Olex2 [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.35398(2)	0.24291(3)	0.06981(2)	0.05665(11)
F1	0.43016(15)	0.6785(4)	0.10640(13)	0.0804(7)
F2	0.45686(15)	0.1285(3)	−0.05643(13)	0.0813(7)
C1	0.4637(2)	0.5881(5)	0.05328(18)	0.0507(8)
C2	0.44073(17)	0.3970(5)	0.02706(17)	0.0450(7)
C3	0.4779(2)	0.3131(5)	−0.02693(19)	0.0507(8)
N1	0.23800(16)	1.0412(5)	0.13553(18)	0.0613(8)
N2	0.0000	0.4289(5)	0.2500	0.0492(10)
C4	0.2113(2)	0.8638(7)	0.1081(2)	0.0661(11)
H4	0.2339	0.8025	0.0704	0.079*
C5	0.1513(2)	0.7648(5)	0.1325(2)	0.0518(9)
H5	0.1335	0.6418	0.1107	0.062*
C6	0.11795(15)	0.8517(4)	0.19028(16)	0.0364(6)
C7	0.14660(17)	1.0359(4)	0.21841(19)	0.0441(7)
H7	0.1257	1.1011	0.2566	0.053*
C8	0.20615(18)	1.1237(5)	0.1901(2)	0.0542(9)
H8	0.2249	1.2475	0.2105	0.065*
C9	0.05280(17)	0.5359(4)	0.22292(17)	0.0422(7)
H9	0.0906	0.4638	0.2042	0.051*
C10	0.05556(17)	0.7480(4)	0.22057(17)	0.0325(6)
C11	0.0000	0.8544(5)	0.2500	0.0328(8)
H11	0.0000	0.9965	0.2500	0.039*

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The 4,3:5,4-terpyridine was purchased from Jinan Heng Hua Technology Co. Ltd. (Shandong, China), and 1,4-diiodotetrafluorobenzene from J&K Scientific Ltd. (Beijing, China). The 4,3:5,4-terpyridine (2.33 mg, 0.01 mmol) and the 1,4-diiodotetrafluorobenzene (4.02 mg, 0.01 mmol) were dissolved in approximately 15 mL of trichloromethane with 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 conditions. After about three days, clear light colourless crystals of title complex were obtained.

Experimental details

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

Comment

There has been considerable progress toward understanding the nature and application of the halogen bond [5–10]. In the present study, we reported the crystal structure of the cocrystal formed between 4,3:5,4-terpyridine and 1,4-diiodotetrafluorobenzene. The molecule 4,3:5,4-terpyridine has three electron-rich nitrogen atoms. Theoretically, it can form three halogen bonds with three different 1,4-diiodotetrafluorobenzene molecules. However, many experimental and theoretical studies have shown that not all the halogen bond acceptors can form halogen bonds with the halogen bond donors. So this work should answer the very interesting question of how many halogen bonds one 4,3:5,4-terpyridine molecule can form in the crystal.

All bond lengths and angles in the title crystal structure are in the normal ranges [10]. The 4,3:5,4-terpyridine molecules and 1,4-diiodotetrafluorobenzene molecules are linked by the halogen bonds with $d(\text{I1} \cdots \text{N1}) = 2.864 \text{ \AA}$ and $\angle(\text{C1} - \text{I1} \cdots \text{N1}) = 177.12^\circ$ to form a 1D zigzag chain. Unexpectedly, the electron-rich N2 atom do not form any non-covalent bonds with other electron-deficient atoms. The 1D zigzag chains are linked through $\pi \cdots \pi$ stacking interactions, C–H $\cdots$ F hydrogen bonds and C–F $\cdots$ π noncovalent interactions to form the 3D structure. Different non-covalent interactions will compete with each other during the crystal growth [11]. Here, it is significant to compare the strength of the C1–I1 $\cdots$ N1 halogen bond with the strength of the $\pi \cdots \pi$ stacking interaction between 4,3:5,4-terpyridine and 1,4-diiodotetrafluorobenzene. According to our quantum chemical calculations at the $\omega\text{B97X-D/def2-TZVPP}$ level of theory [12], the binding energy of the C1–I1 $\cdots$ N1 halogen bond is 6.7 kcal/mol and the binding energy of the $\pi \cdots \pi$

stacking interaction between 4,3:5,4-terpyridine and 1,4-diiodotetrafluorobenzene 9.9 kcal/mol. Note that the reliability of the $\omega\text{B97X-D/def2-TZVPP}$ calculation for the study of the molecular interactions can be found elsewhere [13]. Evidently, the $\pi \cdots \pi$ stacking interaction between 4,3:5,4-terpyridine and 1,4-diiodotetrafluorobenzene is stronger. It is possible that the formation of the stronger $\pi \cdots \pi$ stacking interaction between 4,3:5,4-terpyridine and 1,4-diiodotetrafluorobenzene prevents the further formation of the third halogen bond involving the N2 atom.

As a response to the question of how many halogen bonds can one 4,3:5,4-terpyridine molecule form in the crystal structure, the results of this study clearly show that one 4,3:5,4-terpyridine molecule can form two halogen bonds with two different 1,4-diiodotetrafluorobenzene molecules in the crystal structure.

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