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

Molecular structure of the title complex with displacement ellipsoids draw at the 50% probability level.

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Abstract

$C_{21}H_{11}F_4I_2N_3$, orthorhombic, $Pnma$ (no. 62), $a = 11.0042(4)$ Å, $b = 20.6209(5)$ Å, $c = 9.2371(3)$ Å, $V = 2096.05(11)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0316$, $wR_{ref}(F^2) = 0.0556$, $T = 293(2)$ K.

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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 1,3-diiodotetrafluorobenzene was purchased from J&K Scientific Ltd. (Beijing, China). Both of them were used without further purification. The halogen bond acceptor 4,3':5',4''-terpyridine (2.33 mg, 0.01 mmol) and the halogen bond donor 1,3-diiodotetrafluorobenzene (4.02 mg, 0.01 mmol) were

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.21 × 0.20 × 0.17 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ :	3.05 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
θ_{max} , completeness:	28.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	22,257, 2503, 0.037
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1994
$N(param)_{refined}$:	145
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4]

dissolved in 15 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 at room temperature conditions. After about three days, colorless block crystals of title compound were obtained.

Experimental details

The structure was solved with the SHELXT [3] program using Intrinsic Phasing and refined with the SHELXL [4] refinement package. 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 theoretical and experimental studies of the halogen bonds have attracted considerable attention [5–9]. The halogen bonds in the crystal structure of the cocrystal formed between 4,3':5',4''-terpyridine and 1,4-diiodotetrafluorobenzene have been reported in a previous study [10]. In this work, the cocrystal formed between 4,3':5',4''-terpyridine and 1,3-diiodotetrafluorobenzene was synthesized and the halogen bonds in its crystal structure was investigated.

All bond lengths and angles in the title crystal structure are in the normal ranges. The 4,3':5',4''-terpyridine molecules and 1,3-diiodotetrafluorobenzene molecules are linked

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.78735 (2)	0.39662 (2)	0.40387 (3)	0.05317 (9)
F1	0.7038 (2)	0.2500	0.3986 (3)	0.0510 (7)
F2	1.07476 (18)	0.36309 (10)	0.4135 (2)	0.0690 (6)
F3	1.1960 (2)	0.2500	0.4129 (3)	0.0676 (8)
C9	0.8271 (4)	0.2500	0.4033 (5)	0.0419 (10)
C10	0.8855 (3)	0.30881 (15)	0.4064 (3)	0.0419 (7)
C11	1.0108 (3)	0.30739 (16)	0.4100 (3)	0.0481 (8)
C12	1.0736 (4)	0.2500	0.4106 (5)	0.0494 (12)
N1	0.6466 (3)	0.51087 (14)	0.3922 (4)	0.0630 (8)
N2	0.2858 (4)	0.7500	0.2470 (5)	0.0577 (11)
C1	0.6649 (3)	0.56103 (17)	0.4795 (4)	0.0619 (10)
H1	0.7206	0.5564	0.5545	0.074*
C2	0.6057 (3)	0.61982 (16)	0.4653 (4)	0.0533 (9)
H2	0.6222	0.6533	0.5298	0.064*
C3	0.5224 (3)	0.62892 (15)	0.3557 (4)	0.0427 (7)
C4	0.5012 (3)	0.57571 (17)	0.2666 (4)	0.0583 (9)
H4	0.4445	0.5784	0.1921	0.070*
C5	0.5646 (4)	0.51908 (18)	0.2892 (5)	0.0727 (12)
H5	0.5487	0.4843	0.2281	0.087*
C6	0.5184 (4)	0.7500	0.3608 (5)	0.0421 (11)
H6	0.5960	0.7500	0.4008	0.051*
C7	0.4610 (3)	0.69167 (15)	0.3312 (3)	0.0413 (7)
C8	0.3444 (3)	0.69504 (17)	0.2751 (4)	0.0506 (8)
H8	0.3045	0.6563	0.2557	0.061*

by the halogen bonds with $d(\text{I1}\cdots\text{N1}) = 2.822 \text{ \AA}$ and $\angle(\text{C10}-\text{I1}\cdots\text{N1}) = 177.05^\circ$ to form a zigzag chain. Similar to the case in the crystal structure of the cocrystal formed between 4,3':5',4''-terpyridine and 1,4-diiodotetrafluorobenzene [10], the electron-rich N2 atom does not form any halogen bond. In the crystal structure of the cocrystal formed between 4,3':5',4''-terpyridine and 1,4-diiodotetrafluorobenzene, the zigzag chains are linked mainly through the $\pi\cdots\pi$ stacking interactions to form a 3D structure [10]. In the title structure, there are no $\pi\cdots\pi$ stacking interactions found; the zigzag chains are linked together through the $\text{C8}-\text{H8}\cdots\text{N1}$ and $\text{C6}-\text{H6}\cdots\text{N2}$ hydrogen bonds to form the 3D structure. According to the dispersion-corrected density functional theory calculations at the PBE0-D3/def2-TZVPP level of theory [11, 12], the binding energy of one strong $\text{C6}-\text{H6}\cdots\text{N2}$ hydrogen bond and two weak $\text{C8}-\text{H8}\cdots\text{N1}$ hydrogen bonds formed between two 4,3':5',4''-terpyridine molecules is 7.77 kcal/mol, and the binding energy of one $\text{C10}-\text{I1}\cdots\text{N1}$ halogen bond formed between 4,3':5',4''-terpyridine and 1,3-diiodotetrafluorobenzene is 8.00 kcal/mol. The details and reliability of the PBE0-D3/def2-TZVPP calculations for the study of the non-covalent interactions can be found elsewhere [13–15]. Evidently, the strength of one $\text{C}-\text{I}\cdots\text{N}$ halogen bond is much stronger than the strength of one $\text{C}-\text{H}\cdots\text{N}$ hydrogen bond.

In conclusion, the 4,3':5',4''-terpyridine molecule only forms two strong halogen bonds with two 1,3-diiodotetrafluorobenzene molecules. The third electron-rich nitrogen atom of 4,3':5',4''-terpyridine forms a hydrogen bond with one C–H bond of another 4,3':5',4''-terpyridine molecule.

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