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Halogen bonds in the crystal structure of 1,4-diiodotetrafluorobenzene–1,2-bis(4-pyridyl)propane (1/1), $C_{19}H_{14}F_4I_2N_2$

The crystal structure is shown in the figure. The asymmetric unit is labelled. 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:	Colorless block
Size:	$0.31 \times 0.28 \times 0.05$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	3.18 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω -scans
θ_{max} , completeness:	25.5° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	9761, 1857, 0.034
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1690
$N(\text{param})_{\text{refined}}$:	123
Programs:	Bruker programs [1], SHELX [2, 3], OLEX2 [4]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.41548(2)	0.26813(6)	0.34547(2)	0.05142(13)
F1	0.54774(14)	−0.1618(7)	0.41246(12)	0.0685(8)
F2	0.61004(14)	−0.3697(7)	0.52822(13)	0.0752(8)
C1	0.4665(2)	0.1077(9)	0.43808(18)	0.0424(9)
C2	0.5227(2)	−0.0791(9)	0.45520(19)	0.0444(10)
C3	0.5556(2)	−0.1833(9)	0.5155(2)	0.0481(10)
N1	0.3545(2)	0.5169(8)	0.22681(16)	0.0561(9)
C4	0.2877(2)	0.5791(11)	0.1968(2)	0.0544(11)
H4	0.2568	0.5018	0.2126	0.065*
C5	0.2614(2)	0.7514(9)	0.1435(2)	0.0501(11)
H5	0.2139	0.7879	0.1245	0.060*
C6	0.3051(2)	0.8710(8)	0.11813(17)	0.0382(9)
C7	0.3746(2)	0.8034(10)	0.1494(2)	0.0532(11)
H7	0.4067	0.8764	0.1347	0.064*
C8	0.3963(2)	0.6293(12)	0.2022(2)	0.0636(13)
H8	0.4435	0.5871	0.2220	0.076*
C9	0.2786(2)	1.0550(8)	0.05967(16)	0.0411(9)
H9A	0.3161	1.1791	0.0587	0.049*
H9B	0.2422	1.1861	0.0605	0.049*
C10	0.2500	0.8656(12)	0.0000	0.0432(13)
H10A ^a	0.2133	0.7381	0.0014	0.052*
H10B ^a	0.2867	0.7381	−0.0014	0.052*

^aOccupancy: 0.5.

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Abstract

$C_{19}H_{14}F_4I_2N_2$, monoclinic, $I2/a$ (no. 15), $a = 20.997(2)$ Å, $b = 4.4785(3)$ Å, $c = 23.242(3)$ Å, $\beta = 113.532(14)^\circ$, $V = 2003.8(4)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0684$, $wR_{\text{ref}}(F^2) = 0.0706$, $T = 287$ K.

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Source of material

The 1,4-diiodotetrafluorobenzene and 1,2-bis(4-pyridyl)propane were purchased from Aldrich Chemical Co., and used as received. The halogen bond donor 1,4-diiodotetrafluorobenzene (40.2 mg, 0.1 mmol) and the halogen bond acceptor 1,2-bis(4-pyridyl)propane (19.8 mg, 0.1 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 trichloromethane at room temperature. After a few days, colourless crystals of title complex suitable for single-crystal X-ray diffraction 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 $1.2U_{\text{eq}}(\text{C})$.

Discussion

Besides the hydrogen bond, other noncovalent interactions such as the halogen bond, chalcogen bond and $\pi \cdots \pi$ stacking interaction play an important role in the crystal growth and design [5–11]. All these noncovalent interactions work together to construct the 0D, 1D, 2D, or 3D structures of crystals. At the same time, the competitions between different noncovalent interactions also exist during the formation of the crystals. The most common competition in the crystal engineering involving halogen bond occurs between the halogen bond and the $\pi \cdots \pi$ stacking interaction [12–16]. In a previous paper, we investigated the structural competition between the C—I $\cdots$ O halogen bond and the π – π stacking interaction [13]. The compounds 1,4-diiodotetrafluorobenzene and 1,2-bis(4-pyridyl)propane are good candidates for the formation of the C—I $\cdots$ N halogen bond and the $\pi \cdots \pi$ stacking interaction.

All bond lengths and angles in the title crystal structure are in the normal ranges [16]. The 1,4-diiodotetrafluorobenzene molecules and the 1,2-bis(4-pyridyl)propane molecules are linked by the halogen bonds with $d(\text{I1} \cdots \text{N1}) = 2.769 \text{ \AA}$ and $\angle(\text{C1—I1} \cdots \text{N1}) = 175.72^\circ$ to form a 1D chain structure. The adjacent 1D chains are linked through weak C—H $\cdots$ F hydrogen bonds to form a 3D framework with channels along the *c* axis. According to quantum chemical calculations, the $\pi \cdots \pi$ stacking interaction between two 1,4-diiodotetrafluorobenzene molecules is much weaker than the halogen bond with the type of C—I $\cdots$ N [14, 15]. So, unlike the case in the crystal structure of the cocrystal formed between 1,3,5-trifluoro-2,4,6-triiodobenzene and *N,N*-dimethylformamide, no $\pi \cdots \pi$ stacking interaction between two 1,4-diiodotetrafluorobenzene molecules is found in the crystal structure of the title compound [13].

It is significant to compare the crystal structure of the cocrystal formed between 1,4-diiodotetrafluorobenzene and 1,2-bis(4-pyridyl)propane with the crystal structure of the cocrystal formed between 1,4-diiodotetrafluorobenzene and 4,4'-bipyridine and the crystal structure of the cocrystal formed between 1,4-diiodotetrafluorobenzene and 1,2-bis(4-pyridyl)ethane [11, 12]. In the crystal structures of these cocrystals, different monomers are linked by the C—I $\cdots$ N halogen bonds to form 1D chains. The I $\cdots$ N distance is 2.851 Å in the crystal structure of the cocrystal formed between 1,4-diiodotetrafluorobenzene and 4,4'-bipyridine and 2.793 Å in the crystal structure of the cocrystal formed between 1,4-diiodotetrafluorobenzene and 1,2-bis(4-pyridyl)ethane [11, 12]. Both of them are larger than the I $\cdots$ N distance (2.769 Å) in the crystal structure of the title structure. The shorter I $\cdots$ N distance represents a stronger C—I $\cdots$ N halogen bond. This indicates that the longer the distances between two pyridine rings are, the stronger the C—I $\cdots$ N halogen bonds become. Steric and electronic effects influence the strength of the C—I $\cdots$ N halogen bond and the crystal packing.

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