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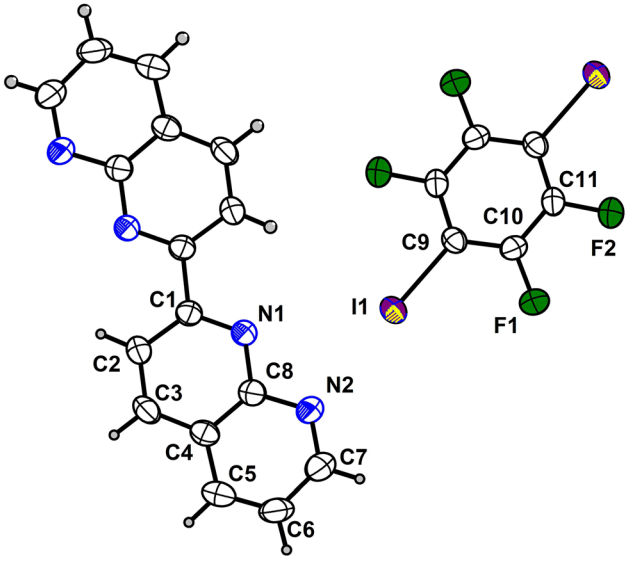
Bifurcated halogen bonds in the crystal structure of 2,2′-bi(1,8-naphthyridine)—1,4-diiodotetrafluorobenzene (1/1), $C_{22}H_{10}F_4I_2N_4$



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Abstract

$C_{22}H_{10}F_4I_2N_4$, monoclinic, $P2_1/c$ (no. 14), a = 9.7940(3) Å, b = 5.34970(10) Å, c = 20.5119(5) Å, β = 101.673(3)°, V = 1052.49(5) Å^3, Z = 2, $R_{gt}(F)$ = 0.0222, w$R_{ref}(F^2)$ = 0.0505, 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.

Table 1: Data collection and handling.

Crystal:	Brown block
Size:	0.27 × 0.25 × 0.24 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	3.04 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	28.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14098, 2416, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2214
$N(param)_{refined}$:	145
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3, 4]

Source of material

The 2,2′-bi(1,8-naphthyridine) (purity > 98%) was bought from J&K Scientific Ltd. (Beijing, China), and 1,4-diiodotetrafluorobenzene (purity > 98%) was purchased from Alfa Chemical Co., Ltd. (Zhengzhou, China). The solvent trichloromethane (analytical grade) was bought from a local chemical company. All of the chemicals were used as received. The crystalline compounds 2,2′-bi(1,8-naphthyridine) (1.29 mg, 0.005 mmol) and 1,4-diiodotetrafluorobenzene (2.01 mg, 0.005 mmol) were dissolved in approximately 10 mL of trichloromethane under gentle stirring. The solution was placed for crystallization by slow evaporation of the solvent at room temperature. After about two days, brown block crystals of title compound were obtained.

Experimental details

All the hydrogen atoms were placed in calculated positions, and then treated as riding atoms in the latter stages of refinement, with U_{iso}(H) set to 1.2U_{eq}(C).

Comment

The halogen bond is one of the most important non-covalent bonds [5–11]. In recent years, the application of the halogen bond has been extended to the fields of medicinal chemistry and advanced materials [8–11]. According to a statistic in 2014, 34% of drugs at the research stage were halogenated drugs [9, 10]. This indicates that the formation probability of the halogen bond in medicinal chemistry is quite large. The important

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

Atom	x	y	z	U_{iso}*/U_{eq}
I1	0.62398 (2)	0.46696 (3)	0.40701 (2)	0.03647 (7)
F1	0.35218 (16)	0.1108 (3)	0.37691 (7)	0.0544 (4)
F2	0.26126 (16)	−0.2467 (3)	0.44727 (8)	0.0530 (4)
C9	0.5491 (2)	0.1881 (4)	0.46221 (11)	0.0325 (5)
C10	0.4271 (3)	0.0595 (5)	0.43829 (12)	0.0355 (6)
C11	0.3794 (2)	−0.1238 (5)	0.47488 (12)	0.0346 (5)
N1	0.8799 (2)	0.9095 (4)	0.42676 (10)	0.0355 (5)
N2	0.7324 (2)	0.8424 (4)	0.32636 (10)	0.0456 (6)
C1	0.9798 (3)	1.0408 (5)	0.46445 (12)	0.0343 (5)
C2	1.0463 (3)	1.2462 (5)	0.44131 (13)	0.0424 (6)
H2	1.1155	1.3341	0.4700	0.051*
C3	1.0077 (3)	1.3140 (5)	0.37630 (13)	0.0451 (6)
H3	1.0514	1.4474	0.3598	0.054*
C4	0.9009 (3)	1.1805 (5)	0.33396 (12)	0.0373 (6)
C5	0.8472 (3)	1.2394 (6)	0.26630 (13)	0.0491 (7)
H5	0.8849	1.3701	0.2458	0.059*
C6	0.7401 (3)	1.1026 (6)	0.23194 (14)	0.0550 (8)
H6	0.7028	1.1389	0.1876	0.066*
C7	0.6864 (3)	0.9064 (6)	0.26389 (14)	0.0542 (8)
H7	0.6130	0.8146	0.2393	0.065*
C8	0.8393 (3)	0.9797 (5)	0.36185 (13)	0.0354 (6)

role of the halogen bond in perovskite solar cells has also been reviewed by Metrangolo and coworkers very recently [11]. In contrast to the conventional monocentric halogen bonds, the bifurcated halogen bonds were less studied [12]. In a very recent study, Wang investigated the bifurcated halogen bonds in the crystal structure of the cocrystal between 2,2′-bi(1,8-naphthyridine) and 1,2-diiodotetrafluorobenzene [12].

All bond lengths and angles in the title crystal structure are in the normal ranges. The 2,2′-bi(1,8-naph thyridine) molecules and 1,4-diiodotetrafluorobenzene molecules are linked together by the bifurcated halogen bonds with d(I1···N1) = 3.412 Å, <(C9–I1···N1) = 139.44°, d(I1···N2) = 2.934 Å and <(C9–I1···N2) = 177.74° to form a zigzag chain. The interaction energy of the bifurcated halogen bond is −10.68 kcal/mol at the PBE0–D3/def2–TZVPP level of theory [13, 14], which is almost the same as the interaction energy of the bifurcated halogen bond in the crystal structure of the cocrystal between 2,2′-bi(1,8-naphthyridine) and 1,2-diiodotetrafluorobenzene [12]. The zigzag chains are stacked together by the $\pi\cdots\pi$ stacking interactions to form a layered structure. At the PBE0–D3/def2–TZVPP level of theory, the $\pi\cdots\pi$ stacking interaction energy between two 2,2′-bi(1,8-naphthyridine) molecules is −6.75 kcal/mol; the $\pi\cdots\pi$ stacking interaction energy between two 1,4-diiodotetrafluorobenzene molecules is −5.72 kcal/mol; the $\pi\cdots\pi$ stacking interaction energy between 2,2′-bi(1,8-naphthyridine) and 1,4-diiodotetrafluorobenzene is −6.77 kcal/mol. Let us add here that previous studies have proved that the PBE0–D3/def2–TZVPP calculations perform remarkably well for the study of the noncovalent interactions [15–17]. Obviously, the bifurcated halogen bonds are much stronger than all of these $\pi\cdots\pi$ stacking interactions. Different layers are linked by C–H···F hydrogen bonds into a 3D architecture.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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