Crystal structure of 1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-iodo-5-amino-1*H*-pyrazole-3-carbonitrile, $C_{11}H_4Cl_2F_3IN_4$

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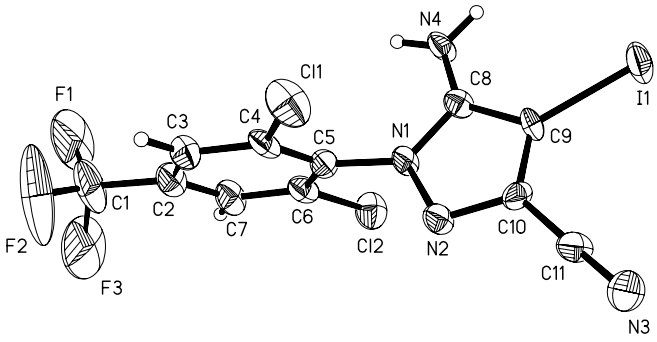

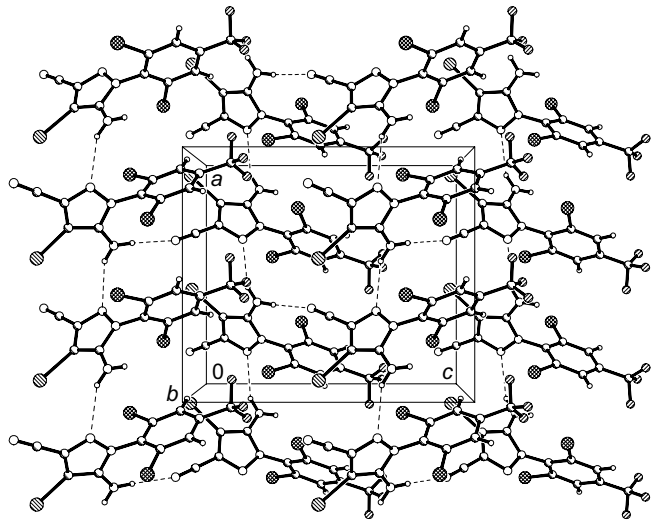

Abstract

$C_{11}H_4Cl_2F_3IN_4$, orthorhombic, *Pna*2$_1$ (no. 33), a = 11.062(2) Å, b = 10.878(2) Å, c = 12.666(2) Å, V = 1524.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.054, $wR_{ref}(F^2)$ = 0.116, T = 298 K.

Source of material

Following the literature method [1], reaction of 2,6-dichloro-4-trifluoromethylaniline (2.5 mmol) with a suspension of nitrosyl sulphuric acid, followed by reaction with a solution of ethyl 2,3-dicyanopropionate (2.5 mmol) in acetic acid, gave 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole (about 2 mmol), which was then stirred with *N*-iodosuccinimide (2.6 mmol) [2] in acetonitrile (8 mL) at room temperature. After being stirred a few minutes, the reaction was monitored by TLC till the complete consumption of the starting materials. Finally, the reaction mixture was evaporated under reduced pressure to provide the required crude product, which was then partitioned between dichloromethane and water. The organic phase was evaporated under reduced pressure to give the title compound (yield 77.4 %). Colorless single crystals suitable for X-ray analysis were obtained by slow evaporation of an anhydrous ethanol/acetone solution (2:1) (m.p. 491-493 K). IR, ^{1}H, and ^{13}C NMR data are available in the CIF.

Experimental details

The H atoms bound to C atoms were positioned geometrically and allowed to ride on their parent atoms at distances of C_{sp2}—H of 0.93 Å. The positions of the H atoms bound to N atoms were refined using N—H distance restraints of 0.86(2) Å. All U_{iso}(H) values were set at 1.2U_{eq}(parent atom). The large U_{ii} of C1 as compared to neighbors may be attributed to the three disordered fluorine atoms. We refined the structure by taking into account the presence of disorder, but failed. The inability to account for the electron-density distribution in the vicinity of CF_3 group limits the overall precision of the structure.

Discussion

The title compound is similar to the very effective insecticides used to treat animals such as cows and sheeps [2,3] and its structure is reported here. The molecule contains two essentially planar rings (figure, top). All bond lengths and angles are in agreement with those observed in similar compounds [4,5]. The dihedral angle between the pyrazole and the benzene rings is 82.2(2)°. In the crystal packing (figure, bottom), there are two kinds of intermolecular N–H···N hydrogen bonds. N4–H4A···N2 interactions form ribbons along [100] and these ribbons are linked to form a three-dimensional network via N4–H4B···N3 hydrogen bonds.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.11 × 0.13 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	24.80 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, ω/φ
$2\theta_{max}$:	50.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7688, 2229
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2152
$N(param)_{refined}$:	196
Programs:	SHELXS-97 [6], SHELXL-97 [7]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3)	4*a*	0.1682	0.0770	0.5628	0.070
H(7)	4*a*	0.0188	0.3979	0.4785	0.068
H(4A)	4*a*	0.444(6)	0.34(1)	0.185(8)	0.069
H(4B)	4*a*	0.37(1)	0.36(1)	0.283(4)	0.069

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	4*a*	0.43450(6)	0.21839(6)	–0.03816(6)	0.0731(4)	0.0784(4)	0.0477(4)	–0.0072(3)	0.0289(4)	–0.0143(5)
Cl(1)	4*a*	0.2826(3)	–0.0062(2)	0.3807(3)	0.080(2)	0.056(1)	0.100(3)	0.019(1)	0.027(2)	0.005(2)
Cl(2)	4*a*	0.0803(3)	0.4209(3)	0.2672(3)	0.073(2)	0.063(2)	0.061(2)	0.016(1)	0.007(1)	0.002(1)
F(1)	4*a*	0.094(1)	0.332(2)	0.7013(9)	0.22(2)	0.33(2)	0.069(7)	–0.12(1)	0.066(9)	–0.10(1)
F(2)	4*a*	0.031(2)	0.156(1)	0.698(1)	0.46(3)	0.13(1)	0.10(1)	0.04(1)	0.16(1)	0.011(8)
F(3)	4*a*	–0.068(1)	0.300(2)	0.648(1)	0.16(1)	0.44(3)	0.085(9)	0.08(1)	0.064(9)	–0.03(1)
N(1)	4*a*	0.2116(6)	0.1900(6)	0.2296(6)	0.041(4)	0.044(4)	0.039(5)	–0.009(3)	0.013(4)	–0.024(3)
N(2)	4*a*	0.1527(6)	0.1043(7)	0.1692(7)	0.042(4)	0.049(4)	0.047(5)	–0.008(3)	0.011(4)	–0.019(4)
N(3)	4*a*	0.1442(9)	–0.039(1)	–0.0696(8)	0.069(6)	0.110(7)	0.066(8)	–0.008(6)	0.009(5)	–0.047(7)
N(4)	4*a*	0.3802(7)	0.3282(8)	0.2203(8)	0.041(4)	0.064(5)	0.051(6)	–0.018(4)	0.020(4)	–0.029(5)
C(1)	4*a*	0.043(2)	0.256(2)	0.649(1)	0.14(2)	0.088(9)	0.07(1)	–0.027(9)	0.06(1)	–0.024(9)
C(2)	4*a*	0.088(1)	0.240(1)	0.537(1)	0.064(7)	0.063(6)	0.047(6)	–0.020(5)	0.013(5)	–0.022(6)
C(3)	4*a*	0.1534(9)	0.137(1)	0.512(1)	0.057(6)	0.067(7)	0.050(7)	–0.011(5)	0.006(6)	0.007(5)
C(4)	4*a*	0.1974(8)	0.1226(9)	0.4108(9)	0.031(5)	0.051(5)	0.056(7)	–0.003(4)	0.016(4)	–0.009(5)
C(5)	4*a*	0.1745(8)	0.2084(9)	0.3353(8)	0.045(5)	0.057(6)	0.037(6)	–0.015(4)	0.004(4)	–0.014(5)
C(6)	4*a*	0.1086(8)	0.3126(8)	0.3622(9)	0.038(4)	0.040(4)	0.055(7)	–0.006(4)	0.008(4)	–0.013(5)
C(7)	4*a*	0.0641(9)	0.3285(8)	0.462(1)	0.062(5)	0.053(5)	0.055(6)	0.002(4)	0.021(5)	–0.019(8)
C(8)	4*a*	0.3092(7)	0.2408(7)	0.1788(8)	0.038(5)	0.035(4)	0.049(6)	0.005(4)	0.006(4)	–0.006(4)
C(9)	4*a*	0.3111(8)	0.1839(8)	0.0796(8)	0.041(5)	0.047(5)	0.035(5)	0.004(4)	0.019(4)	–0.004(4)
C(10)	4*a*	0.2140(8)	0.1044(8)	0.0789(8)	0.036(5)	0.057(5)	0.039(5)	0.010(4)	–0.005(4)	–0.022(5)
C(11)	4*a*	0.1755(8)	0.0213(9)	–0.002(1)	0.036(5)	0.069(6)	0.066(8)	–0.002(4)	0.008(5)	–0.045(6)

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