Crystal structure of 1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-5-((3-bromophenyl)methyleneimino)-1*H*-pyrazole-3-carbonitrile, $C_{18}H_8BrCl_2F_3N_4$

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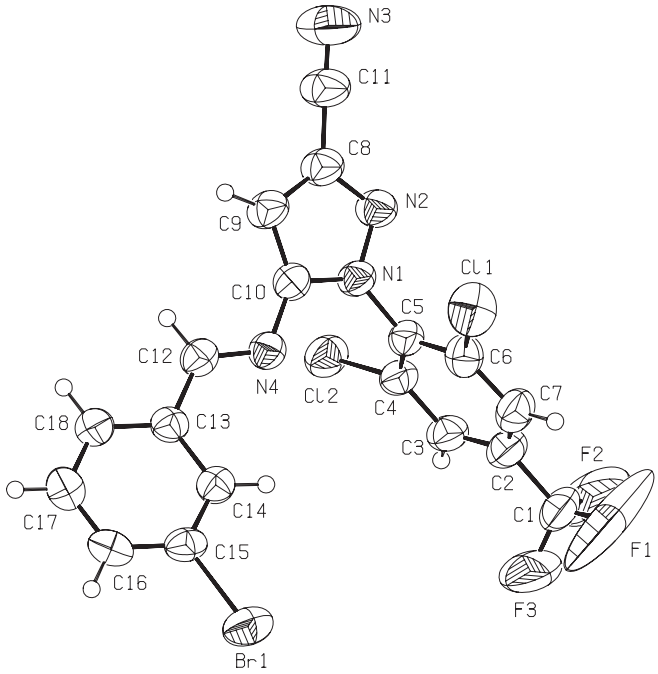

Abstract

$C_{18}H_8BrCl_2F_3N_4$, monoclinic, $P12_1/c1$ (no. 14), a = 13.064(1) Å, b = 14.692(1) Å, c = 9.9933(9) Å, β = 101.361(2)°, V = 1880.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.049, $wR_{ref}(F^2)$ = 0.145, T = 273 K.

Source of material

Following the literature method [1], the reaction of 2,6-dichloro-4-(trifluoromethyl)aniline (10 mmol, 2.3 g) with a suspension of sodium nitrite (10 mmol, 0.69 g) and sulfuric acid (3 ml), followed by reaction with a solution of ethyl 2,3-dicyanopropionate (10 mmol, 1.52 g) in acetic acid (5 ml), gave 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-pyrazole. The compound was then reacted with 3-bromobenzaldehyde (10 mmol, 1.85 g) to give the title compound. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a methanol solution.

Experimental details

The large displacement parameters of the fluorine atoms represent the rotational disorder. All H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of d(C—H) = 0.93 Å and d(N—H) = 0.86 Å with $U_{iso} = 1.2U_{eq}$(parent atom).

Discussion

The title compound is an important intermediate in synthesis of trifluoromethyl-containing pyrazole derivatives, which are good insecticides [2]. Trifluoromethylated compounds have been found diverse applications in the areas of materials science, agrochemistry and biomedical chemistry due to their unique chemical, physical and biological properties [3,4]. In order to continue investigations of such trifluoromethyl-containing pyrazoles, the title compound was synthesized and its crystal structure determined.

The title compound consists of three different rings, the first phenyl ring (C2/C3/C4/C5/C6/C7), the second phenyl ring (C13/C14/C15/C165/C17/C18) and the pyrazolyl ring (N1/N2/C8/C9/C10), which are all almost planar. The dihedral angles between pyrazolyl ring and phenyl (C2 - C7) and phenyl (C13 - C18) rings are 86.7° and 153.5°, respectively. In the crystal structure, all bond lengths and angles in are normal. Furthermore, there are no obvious π-π interactions between pyrazolyl ring and phenyl rings.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.17 × 0.24 × 0.38 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	25.10 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, φ/ω
$2\theta_{max}$:	50.48°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9892, 3388
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2681
$N(param)_{refined}$:	253
Programs:	SHELXS-97 [5], SHELXL-97 [6], SHELXTL [7]

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

Atom	Site	x	y	z	U_{iso}
H(3)	4*e*	0.6826	0.8206	0.4275	0.066
H(7)	4*e*	0.5152	0.6878	0.6637	0.073
H(9)	4*e*	0.8890	0.3590	0.5194	0.067
H(12)	4*e*	1.0091	0.4691	0.6580	0.058
H(14)	4*e*	0.9290	0.6287	0.8882	0.056
H(16)	4*e*	1.2008	0.6318	1.1585	0.071
H(17)	4*e*	1.2721	0.5328	1.0218	0.078
H(18)	4*e*	1.1726	0.4808	0.8196	0.066

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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}
Br(1)	4*e*	1.00047(4)	0.71947(3)	1.14718(5)	0.0923(4)	0.0588(3)	0.0653(3)	–0.0019(2)	0.0296(3)	–0.0125(2)
Cl(1)	4*e*	0.5912(1)	0.5091(1)	0.6712(1)	0.0828(8)	0.0783(8)	0.0789(8)	0.0016(6)	0.0282(7)	0.0220(6)
Cl(2)	4*e*	0.80475(9)	0.68624(8)	0.3426(1)	0.0681(7)	0.0583(6)	0.0748(7)	–0.0026(5)	0.0307(6)	–0.0055(5)
F(1)	4*e*	0.4743(8)	0.8488(4)	0.641(1)	0.40(1)	0.106(4)	0.49(1)	0.113(6)	0.37(1)	0.073(6)
F(2)	4*e*	0.4882(5)	0.8884(4)	0.4587(6)	0.223(6)	0.137(4)	0.173(5)	0.125(4)	–0.060(4)	–0.052(3)
F(3)	4*e*	0.5977(4)	0.9166(3)	0.6172(7)	0.141(4)	0.107(3)	0.304(7)	0.057(3)	–0.055(5)	–0.119(4)
N(1)	4*e*	0.7382(2)	0.5224(2)	0.4818(3)	0.052(2)	0.040(2)	0.050(2)	0.007(1)	0.004(2)	–0.002(1)
N(2)	4*e*	0.6882(3)	0.4689(2)	0.3803(3)	0.059(2)	0.046(2)	0.055(2)	0.005(2)	0.002(2)	–0.000(2)
N(3)	4*e*	0.6932(5)	0.2658(3)	0.2188(6)	0.137(5)	0.060(3)	0.095(4)	0.017(3)	–0.035(3)	–0.017(3)
N(4)	4*e*	0.8835(3)	0.5319(2)	0.6645(3)	0.049(2)	0.044(2)	0.051(2)	0.005(1)	0.007(2)	0.001(1)
C(1)	4*e*	0.5376(4)	0.8547(4)	0.5667(6)	0.066(3)	0.087(4)	0.086(4)	0.033(3)	0.002(3)	–0.030(3)
C(2)	4*e*	0.5898(4)	0.7664(3)	0.5477(5)	0.061(3)	0.056(3)	0.058(3)	0.015(2)	0.005(2)	–0.010(2)
C(3)	4*e*	0.6652(3)	0.7669(3)	0.4671(4)	0.061(3)	0.042(2)	0.059(3)	0.006(2)	0.005(2)	–0.005(2)
C(4)	4*e*	0.7135(3)	0.6865(3)	0.4472(4)	0.052(2)	0.047(2)	0.047(2)	0.003(2)	0.011(2)	–0.007(2)
C(5)	4*e*	0.6903(3)	0.6062(3)	0.5074(4)	0.044(2)	0.045(2)	0.047(2)	0.007(2)	0.003(2)	–0.004(2)
C(6)	4*e*	0.6175(3)	0.6076(3)	0.5909(4)	0.050(2)	0.061(3)	0.049(2)	0.005(2)	0.007(2)	0.006(2)
C(7)	4*e*	0.5657(4)	0.6874(3)	0.6098(5)	0.058(3)	0.073(3)	0.055(2)	0.012(2)	0.017(2)	–0.006(2)
C(8)	4*e*	0.7482(3)	0.3954(3)	0.3895(4)	0.065(3)	0.042(2)	0.060(3)	0.005(2)	0.006(2)	–0.001(2)
C(9)	4*e*	0.8362(3)	0.4018(3)	0.4945(4)	0.063(3)	0.043(2)	0.056(2)	0.013(2)	0.002(2)	0.001(2)
C(10)	4*e*	0.8274(3)	0.4852(3)	0.5523(4)	0.049(2)	0.044(2)	0.047(2)	0.002(2)	0.010(2)	0.002(2)
C(11)	4*e*	0.7182(4)	0.3228(3)	0.2945(5)	0.086(3)	0.047(3)	0.074(3)	0.011(2)	–0.012(3)	–0.005(2)
C(12)	4*e*	0.9781(3)	0.5107(3)	0.7079(4)	0.052(2)	0.044(2)	0.050(2)	0.003(2)	0.015(2)	0.002(2)
C(13)	4*e*	1.0407(3)	0.5485(2)	0.8324(4)	0.049(2)	0.039(2)	0.049(2)	–0.005(2)	0.013(2)	0.001(2)
C(14)	4*e*	0.9977(3)	0.6091(2)	0.9144(4)	0.051(2)	0.040(2)	0.050(2)	–0.001(2)	0.013(2)	0.004(2)
C(15)	4*e*	1.0582(3)	0.6388(3)	1.0331(4)	0.063(3)	0.037(2)	0.053(2)	–0.009(2)	0.020(2)	–0.004(2)
C(16)	4*e*	1.1613(4)	0.6110(3)	1.0765(5)	0.063(3)	0.054(2)	0.058(3)	–0.015(2)	0.005(2)	–0.008(2)
C(17)	4*e*	1.2032(3)	0.5520(3)	0.9952(5)	0.049(2)	0.067(3)	0.076(3)	–0.003(2)	0.006(2)	–0.005(2)
C(18)	4*e*	1.1435(3)	0.5208(3)	0.8738(4)	0.053(2)	0.052(2)	0.060(3)	–0.002(2)	0.015(2)	–0.007(2)

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