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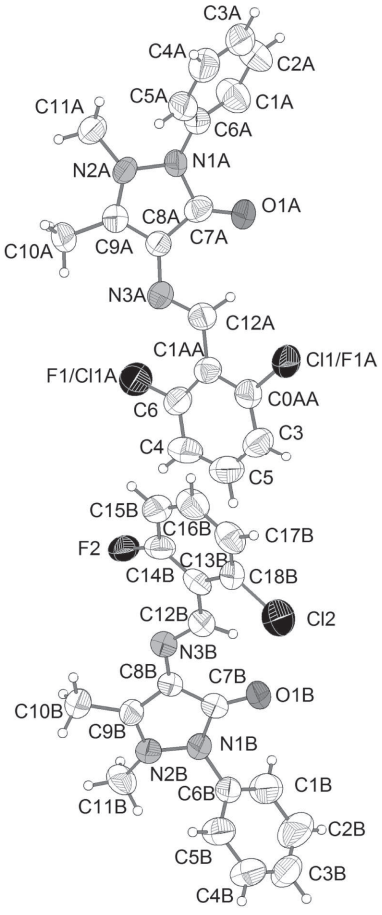
Crystal structure of 4-[(*E*)-(2-chloro-6-fluorobenzylidene)amino]-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one, $C_{18}H_{15}ClFN_3O$



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Abstract

$C_{18}H_{15}ClFN_3O$, monoclinic, $P2_1/c$ (no. 14), $a = 7.5459(3)$ Å, $b = 25.4267(9)$ Å, $c = 17.0478(6)$ Å, $\beta = 91.718(2)°$, $V = 3269.4(2)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0669$, $wR_{ref}(F^2) = 0.1263$, $T = 100$ K.

CCDC no.: 1435621

The asymmetric unit of the title structure is shown in the figure. Tables 1–3 contain details of the methods used and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless, block, size 0.212×0.322×0.451 mm
Wavelength:	CuK_α radiation (1.54178 Å)
μ:	22.48 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω scans
$2\theta_{max}$:	124.97°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	21227, 5127
$N(param)_{refined}$:	431
Programs:	Bruker programs [13], SHELX [14]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1B)	4*e*	0.8541	0.0334	0.4044	0.103
H(2B)	4*e*	0.8410	−0.0434	0.4788	0.135
H(3B)	4*e*	0.5911	−0.0937	0.4736	0.112
H(4B)	4*e*	0.3567	−0.0713	0.3926	0.113
H(5B)	4*e*	0.3636	0.0059	0.3198	0.091
H(10A)	4*e*	0.3964	0.1762	0.1383	0.103
H(10B)	4*e*	0.3526	0.1174	0.1183	0.103
H(10C)	4*e*	0.5420	0.1399	0.1032	0.103
H(11A)	4*e*	0.7284	0.0426	0.1675	0.108
H(11B)	4*e*	0.5336	0.0369	0.1340	0.108
H(11C)	4*e*	0.5995	0.0019	0.2048	0.108

Table 2 (continued)

Atom	Site	x	y	z	U_{iso}
H(12B)	4e	0.5070	0.2171	0.3951	0.071
H(15B)	4e	0.3676	0.3998	0.2619	0.088
H(16B)	4e	0.2355	0.4258	0.3763	0.097
H(17B)	4e	0.1990	0.3662	0.4767	0.087
H(1A)	4e	1.3034	0.7322	0.3904	0.109
H(2A)	4e	1.3025	0.8106	0.4595	0.125
H(3A)	4e	1.0661	0.8667	0.4480	0.108
H(4A)	4e	0.8243	0.8443	0.3694	0.104
H(5A)	4e	0.8202	0.7648	0.3032	0.086
H(10D)	4e	0.8383	0.5900	0.1251	0.102
H(10E)	4e	0.9862	0.6255	0.0900	0.102
H(10F)	4e	0.7975	0.6488	0.1041	0.102
H(11D)	4e	1.0334	0.7641	0.1833	0.103
H(11E)	4e	0.9984	0.7238	0.1150	0.103
H(11F)	4e	1.1827	0.7247	0.1600	0.103
H(12A)	4e	0.9493	0.5532	0.3845	0.070
H(3)	4e	0.7285	0.3971	0.4809	0.089
H(4)	4e	0.8599	0.3641	0.2610	0.094
H(5)	4e	0.7682	0.3371	0.3832	0.099

Source of material

2-Chloro-6-fluorobenzaldehyde (1.59 g, 0.01 mol) was added to a solution of 4-amino-1-phenyl-2,3-dimethyl-3-pyrazolin-5-one (2.03 g, 0.01 mol), in ethanol (10 mL) and the reaction mixture was heated under reflux for 2 h. On cooling, the precipitated crude product was filtered, dried and crystallized from ethanol to yield 2.82 g (82%) of the title compound ($C_{18}H_{15}ClFN_3O$) as colourless block crystals. M.P.: 428–430 K. ^{1}H NMR (DMSO-d_6, 500.13 MHz): $\delta = 2.43$ (s, 3H, CH_3), 3.23 (s, 3H, CH_3), 7.28–7.32 (m, 1H, Ar—H), 7.40–7.43 (m, 5H, Ar—H), 7.45—7.56 (m, 2H, Ar—H), 9.81 (s, 1H, CH=N). ^{13}C NMR (DMSO-d_6, 125.76 MHz): $\delta = 9.63$ (CH_3), 34.95 (CH_3), 115.51, 116.09, 125.03, 126.18, 127.20, 129.14, 131.14, 133.80, 134.23, 147.68, 152.49, 158.99 (Ar—C & Pyrazolone-C), 159.64 (C=O), 161.68 (CH=N).

Experimental details

The hydrogen atoms were placed on calculated positions with the help of the SHELX program (AFIX 43 or 137 option) [14].

Table 3: Fractional coordinates and atomic displacement parameters (Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(2)	4e	0.2865(2)	0.26236(6)	0.49696(8)	0.141(2)	0.103(1)	0.077(1)	−0.007(1)	0.009(1)	−0.011(1)
F(2)	4e	0.5060(3)	0.31255(9)	0.2256(1)	0.100(2)	0.048(2)	0.068(2)	−0.004(2)	0.015(2)	0.000(1)
O(1B)	4e	0.6257(4)	0.1343(1)	0.4164(2)	0.106(3)	0.055(2)	0.050(2)	−0.002(2)	−0.015(2)	−0.005(2)
N(1B)	4e	0.6170(5)	0.0748(2)	0.3128(2)	0.073(3)	0.050(3)	0.048(3)	0.000(2)	−0.004(2)	0.003(2)
N(2B)	4e	0.5490(5)	0.0762(2)	0.2357(2)	0.073(3)	0.046(3)	0.051(3)	−0.003(2)	0.001(2)	−0.001(2)
N(3B)	4e	0.4630(5)	0.2088(2)	0.2844(2)	0.060(3)	0.053(3)	0.055(3)	−0.005(2)	0.000(2)	−0.001(2)
C(1B)	4e	0.7526(8)	0.0126(2)	0.4025(3)	0.081(5)	0.075(5)	0.100(5)	−0.007(4)	−0.021(4)	0.013(4)
C(2B)	4e	0.745(1)	−0.0334(3)	0.4469(4)	0.128(7)	0.089(6)	0.118(6)	0.010(5)	−0.023(5)	0.040(5)
C(3B)	4e	0.597(1)	−0.0634(2)	0.4433(3)	0.143(7)	0.069(5)	0.068(5)	0.003(5)	0.013(5)	0.016(4)
C(4B)	4e	0.4562(9)	−0.0497(2)	0.3957(4)	0.117(6)	0.068(5)	0.099(5)	−0.019(4)	0.010(4)	0.013(4)
C(5B)	4e	0.4603(7)	−0.0038(2)	0.3517(3)	0.077(5)	0.060(4)	0.090(5)	−0.004(3)	0.000(3)	0.004(3)
C(6B)	4e	0.6092(8)	0.0269(2)	0.3561(3)	0.073(4)	0.046(3)	0.052(4)	0.002(3)	−0.003(3)	−0.002(3)
C(7B)	4e	0.5921(6)	0.1248(2)	0.3465(3)	0.061(4)	0.051(4)	0.058(4)	−0.007(3)	−0.002(3)	−0.003(3)
C(8B)	4e	0.5207(6)	0.1565(2)	0.2833(3)	0.056(4)	0.046(3)	0.052(3)	−0.005(3)	−0.003(3)	0.000(3)
C(9B)	4e	0.5022(6)	0.1254(2)	0.2179(3)	0.057(4)	0.059(4)	0.044(3)	−0.007(3)	0.005(3)	0.003(3)
C(10B)	4e	0.4431(6)	0.1411(2)	0.1373(2)	0.085(4)	0.067(4)	0.054(3)	−0.002(3)	0.001(3)	0.006(3)
C(11B)	4e	0.6077(6)	0.0359(2)	0.1808(2)	0.087(4)	0.067(4)	0.063(3)	0.001(3)	0.007(3)	−0.021(3)
C(12B)	4e	0.4642(6)	0.2338(2)	0.3498(3)	0.065(4)	0.057(4)	0.057(3)	−0.002(3)	−0.002(3)	−0.003(3)
C(13B)	4e	0.3993(6)	0.2884(2)	0.3548(3)	0.057(4)	0.054(4)	0.065(4)	−0.003(3)	−0.009(3)	−0.018(3)
C(14B)	4e	0.4179(7)	0.3250(2)	0.2953(3)	0.067(4)	0.043(3)	0.086(4)	−0.004(3)	−0.016(3)	0.003(3)
C(15B)	4e	0.3556(7)	0.3760(2)	0.3027(3)	0.084(5)	0.060(4)	0.075(4)	−0.005(3)	−0.010(3)	0.008(3)
C(16B)	4e	0.2755(7)	0.3914(2)	0.3711(4)	0.086(5)	0.059(4)	0.096(5)	0.018(3)	−0.019(4)	−0.012(4)
C(17B)	4e	0.2550(7)	0.3563(2)	0.4311(3)	0.071(4)	0.073(4)	0.074(4)	0.011(3)	−0.006(3)	−0.020(3)
C(18B)	4e	0.3188(7)	0.3063(2)	0.4224(3)	0.079(4)	0.064(4)	0.051(4)	−0.002(3)	−0.009(3)	0.004(3)
O(1A)	4e	1.0662(4)	0.6351(1)	0.4036(2)	0.112(3)	0.064(2)	0.053(2)	−0.003(2)	−0.021(2)	0.010(2)
N(1A)	4e	1.0601(5)	0.6926(2)	0.2985(2)	0.074(3)	0.052(3)	0.046(3)	0.002(2)	−0.013(2)	0.001(2)
N(2A)	4e	0.9921(5)	0.6909(2)	0.2213(2)	0.071(3)	0.049(3)	0.044(3)	0.005(2)	0.006(2)	0.009(2)
N(3A)	4e	0.9082(5)	0.5586(2)	0.2734(2)	0.057(3)	0.056(3)	0.055(3)	0.005(2)	−0.003(2)	0.006(2)
C(1A)	4e	1.2061(8)	0.7546(2)	0.3863(3)	0.084(5)	0.088(5)	0.099(5)	0.006(4)	−0.020(4)	−0.016(4)
C(2A)	4e	1.2055(9)	0.8016(3)	0.4272(4)	0.117(7)	0.096(6)	0.099(5)	−0.026(5)	−0.018(4)	−0.023(5)
C(3A)	4e	1.065(1)	0.8350(2)	0.4208(3)	0.148(8)	0.070(5)	0.054(4)	−0.001(5)	0.018(4)	−0.011(4)

Table 3 (continued)

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(4A)	4*e*	0.9206(9)	0.8216(2)	0.3741(3)	0.120(6)	0.070(5)	0.071(5)	0.021(4)	0.005(4)	0.000(4)
C(5A)	4*e*	0.9189(7)	0.7743(2)	0.3340(3)	0.090(5)	0.060(4)	0.066(4)	0.003(3)	−0.002(3)	−0.008(3)
C(6A)	4*e*	1.0614(8)	0.7415(2)	0.3396(3)	0.076(5)	0.052(4)	0.054(4)	0.000(3)	−0.002(3)	0.000(3)
C(7A)	4*e*	1.0336(6)	0.6438(2)	0.3336(3)	0.061(4)	0.050(4)	0.069(4)	0.005(3)	−0.002(3)	0.010(3)
C(8A)	4*e*	0.9617(6)	0.6113(2)	0.2708(3)	0.061(4)	0.047(3)	0.049(3)	0.001(3)	0.003(3)	−0.002(3)
C(9A)	4*e*	0.9450(6)	0.6409(2)	0.2046(3)	0.053(4)	0.058(4)	0.052(3)	0.005(3)	0.002(3)	−0.001(3)
C(10A)	4*e*	0.8865(6)	0.6249(2)	0.1237(2)	0.091(4)	0.064(4)	0.048(3)	0.001(3)	−0.005(3)	−0.008(3)
C(11A)	4*e*	1.0572(6)	0.7291(2)	0.1651(2)	0.077(4)	0.064(4)	0.064(3)	−0.002(3)	0.005(3)	0.012(3)
C(12A)	4*e*	0.9129(6)	0.5347(2)	0.3398(3)	0.063(4)	0.051(3)	0.063(4)	0.007(3)	0.000(3)	−0.002(3)
C(0AA)	4*e*	0.7997(6)	0.4603(2)	0.4185(3)	0.063(4)	0.064(4)	0.059(4)	0.001(3)	−0.003(3)	0.001(3)
C(1AA)	4*e*	0.8628(6)	0.4791(2)	0.3477(3)	0.053(4)	0.050(3)	0.062(4)	0.004(3)	−0.003(3)	0.005(3)
C(6)	4*e*	0.8857(7)	0.4404(2)	0.2914(3)	0.074(4)	0.060(4)	0.062(4)	0.000(3)	0.004(3)	0.007(3)
C(3)	4*e*	0.7668(6)	0.4080(2)	0.4322(3)	0.070(4)	0.078(5)	0.076(4)	−0.009(3)	0.000(3)	0.018(4)
C(4)	4*e*	0.8477(7)	0.3882(2)	0.3016(3)	0.081(4)	0.056(4)	0.099(5)	−0.003(3)	0.000(4)	−0.009(4)
C(5)	4*e*	0.7907(7)	0.3725(2)	0.3740(4)	0.079(5)	0.063(4)	0.104(5)	−0.010(3)	−0.012(4)	0.009(4)
Cl(1)[a]	4*e*	0.7595(2)	0.50329(6)	0.48991(8)	0.115(2)	0.081(2)	0.056(1)	−0.003(1)	0.011(1)	0.001(1)
F(1)[a]	4*e*	0.9631(3)	0.45536(8)	0.2158(1)	0.134(2)	0.070(2)	0.077(2)	0.009(2)	0.011(2)	−0.005(1)
F(1A)[b]	4*e*	0.7595(2)	0.50329(6)	0.48991(8)	0.141(2)	0.103(1)	0.077(1)	−0.007(1)	0.009(1)	−0.011(1)
Cl(1A)[b]	4*e*	0.9631(3)	0.45536(8)	0.2158(1)	0.134(2)	0.070(2)	0.077(2)	0.009(2)	0.011(2)	−0.005(1)

[a]Disordered, occupancy factor: 0.768(6).
[b]Disordered, occupancy factor: 0.232(6).

The atoms Cl1/Cl1A and F1/F1A are disordered over two positions with occupancy factors of 0.768(6) (Cl1, F1) and 0.232(6) (Cl1A, F1A).

Discussion

Pyrazolone derivatives as phenazone, metamizole, aminophenazone and propyphenazone have long been utilized as analgesic, anti-inflammatory and antipyretic drugs [1–5]. In addition, several pyrazolone derivatives were reported to exhibit marked antimicrobial [6–8], herbicidal [9] and anti-HIV [10] activities. Moreover, the pyrazolone derivative edaravone (5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one; MCI-186) was discovered as a radical scavenger that interrupt the peroxidative chain reactions and membrane disintegrations associated with cerebral ischemia [11, 12]. In the present study, we describes the synthesis, spectroscopy and crystal structure of the title pyrazolone Schiff's base as a precursor to potential bioactive agents.

In the title compound $C_{18}H_{15}ClFN_3O$, the asymmetric unit contain two independent molecules. The pyrazol-5-one ring (N1/N2/C7/C8/C9) makes the dihedral angles of 59.84(2)° and 84.16(5)° with the phenyl ring (C1—C6) in molecules A and B, respectively. The packing structure shows no classical hydrogen bonds but at least one non-classical hydrogen bond (C17A—H17B$\cdots$O1A with symmetry code: $-x+2$, $-y+1$, $-z+1$) is present.

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