Crystal structure of 9-benzyl-6-ethoxy-7-ethyl-2-phenyl-7,9-dihydropurin-8-one, $C_{22}H_{22}N_4O_2$

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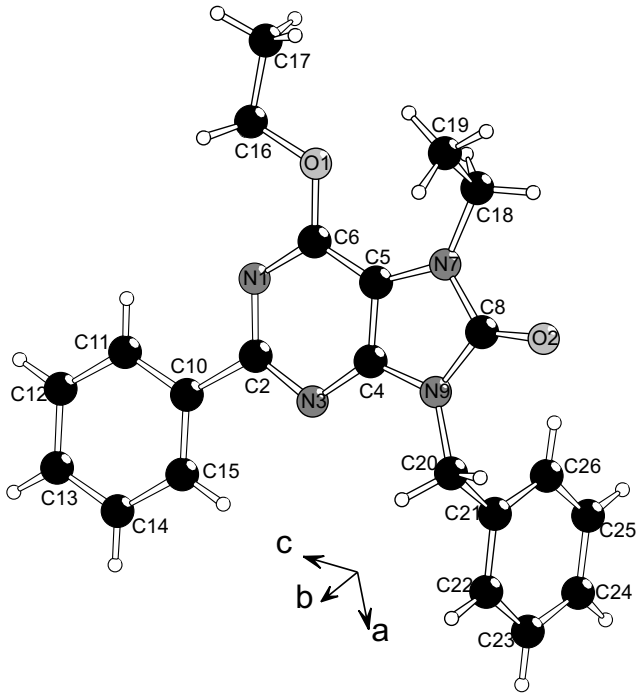

Abstract

$C_{22}H_{22}N_4O_2$, monoclinic, *C*12/*c*1 (No. 15), $a = 22.44(1)$ Å, $b = 7.878(2)$ Å, $c = 23.295(6)$ Å, $\beta = 97.75(3)°$, $V = 4080.9$ Å^3, $Z = 8$, $R_{gt}(F) = 0.045$, $wR_{ref}(F^2) = 0.131$, $T = 295$ K.

Source of material

Condensation of benzamidine hydrochloride with diethylmalonate yielded 2-phenyl-4-hydroxypyrimidin-6-one as described [1]. Bischlorination followed by partial hydrolysis resulted in 4-chloro-2-phenyl-1*H*-pyrimidin-6-one [1,2], which was subjected to nucleophilic substitution of the chlorine atom by benzylamine [3]. C_5-Nitrosation and subsequent reduction of the nitroso group yielded 5-amino-6-benzylamino-2-phenyl-1*H*-pyrimidin-6-one. Reaction with ethylchloroformate followed by ring closure with sodium hydride gave 9-benzyl-2-phenyl-7,9-dihydro-1*H*-purin-6,8-dione [4], which was alkylated by an excess of bromoethane results in the title compound [5]. Crystals were obtained by dissolution in dimethylformamide : water (1 : 1, v/v) and slow evaporation of the solvent over a period of several months.

Experimental details

Hydrogen positions were calculated by SHELXL-97 and refined in the riding model, i.e. the coordinates 'ride', but not so the s.o.f. or U_{iso}. Consideration of the C17 hydrogens decrease the *R* values significantly: $R_{gt}(F)$ from 0.048 to 0.045 and $wR_{ref}(F^2)$ from 0.143 to 0.131.

Discussion

The structure consists of one molecule per asymmetric unit and is held together by van der Waals forces. All intramolecular bond lengths are normal, except C16—C17 (1.447 Å) which is shortened due to a disordered C17 (a possible split position, for clarity, has not been considered in the refinement). The best fit results were obtained for a structure model with one methyl group (C19) assumed ideally disordered, i.e. with two positions rotated by 60°. The main part of the molecule consists of an almost planar aromatic system (N1, N3, N7, N9, C2, C4, C5, C6, C8, C10, C11, C12, C13, C14, C15, C16, C17, C18, C20, O1, O2, H11, H12, H13, H14, H15) with an rms value of the deviations from the least squares plane of 0.049 Å. The fact, that the phenyl group $(C10–C15)_{rms} = 0.0013$ Å is twisted by only 2.7(1)° against the plane defined by the purin-8-one complex (N1, N3, N7, N9, C2, C4, C5, C6, C8, O2)$_{rms} = 0.022$ Å, can be attributed to weak electrostatic interactions between (H15···N3) and (H11···N1), both seperated by 2.473(6) Å. The benzyl group $(C20–C26)_{rms}$ = 0.0133 Å is tilted by 76.1(1)° against the plane of the purin-8-one group. The next intermolecular O···H distances exceed 2.58 Å (O2···H20B). The packing scheme of the molecules is characterized by stacking of the main molecular planes approximately perpendicular to [170] and [$\bar{1}$70], respectively, whereas the benzyl group is almost normal to [001].

Table 1. Data collection and handling.

Crystal:	colorless prisma, size 0.4 × 0.6 × 0.8 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	0.80 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-6R, ω
$2\theta_{max}$:	40.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7313, 1924
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1692
$N(param)_{refined}$:	267
Programs:	SHELXS-97 [6], SHELXL-97 [7], DIAMOND [8]

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(11)	8*f*		0.2324	0.0079	0.6111	0.06
H(12)	8*f*		0.2880	0.1226	0.6923	0.07
H(13)	8*f*		0.3776	0.2564	0.6854	0.07
H(14)	8*f*		0.4122	0.2772	0.5968	0.08
H(15)	8*f*		0.3573	0.1611	0.5154	0.06
H(16A)	8*f*		0.0932	–0.1077	0.5403	0.15
H(16B)	8*f*		0.1222	–0.2894	0.5496	0.15
H(17A)	8*f*		0.0129	–0.2561	0.5452	0.54
H(17B)	8*f*		0.0390	–0.4174	0.5180	0.54
H(17C)	8*f*		0.0148	–0.2649	0.4782	0.54
H(18A)	8*f*		0.1013	–0.3515	0.3619	0.08
H(18B)	8*f*		0.1109	–0.3215	0.2972	0.08
H(19A)	8*f*	0.25(4)	0.0664	–0.0338	0.3249	0.10
H(19B)	8*f*	0.25	0.0301	–0.1660	0.3566	0.10
H(19C)	8*f*	0.25	0.0291	–0.1759	0.2893	0.10
H(19D)	8*f*	0.75	0.0173	–0.2167	0.3223	0.10
H(19E)	8*f*	0.75	0.0536	–0.0845	0.2906	0.10
H(19F)	8*f*	0.75	0.0547	–0.0746	0.3579	0.10
H(20A)	8*f*		0.3111	0.1380	0.3508	0.06
H(20B)	8*f*		0.2845	0.0819	0.2881	0.06
H(22)	8*f*		0.4122	0.1210	0.3310	0.10
H(23)	8*f*		0.4960	–0.0376	0.3212	0.13
H(24)	8*f*		0.4885	–0.3262	0.3103	0.11
H(25)	8*f*		0.3970	–0.4552	0.3059	0.09
H(26)	8*f*		0.3120	–0.2957	0.3134	0.06

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}
N(1)	8*f*	0.2012(1)	–0.0744(3)	0.50903(9)	0.056(2)	0.059(2)	0.041(2)	0.007(1)	0.007(1)	0.004(1)
N(3)	8*f*	0.27565(9)	0.0174(3)	0.4515(1)	0.052(1)	0.050(1)	0.040(2)	0.007(1)	0.010(1)	0.002(1)
N(7)	8*f*	0.1626(1)	–0.1736(3)	0.3528(1)	0.051(1)	0.057(2)	0.045(2)	0.005(1)	0.004(1)	–0.001(1)
N(9)	8*f*	0.24992(9)	–0.0444(3)	0.34960(9)	0.053(1)	0.058(1)	0.039(2)	0.007(1)	0.011(1)	0.001(1)
O(1)	8*f*	0.11387(8)	–0.2115(3)	0.46742(8)	0.057(1)	0.097(2)	0.057(1)	–0.012(1)	0.014(1)	0.007(1)
O(2)	8*f*	0.19545(9)	–0.1371(3)	0.26288(9)	0.082(1)	0.083(2)	0.041(1)	0.012(1)	0.006(1)	–0.008(1)
C(2)	8*f*	0.2533(1)	0.0002(3)	0.5018(1)	0.050(2)	0.045(2)	0.045(2)	0.010(1)	0.008(2)	0.006(1)
C(4)	8*f*	0.2398(1)	–0.0480(3)	0.4067(1)	0.052(2)	0.045(2)	0.038(2)	0.013(1)	0.010(2)	0.003(1)
C(5)	8*f*	0.1859(1)	–0.1278(3)	0.4090(1)	0.048(2)	0.047(2)	0.040(2)	0.008(1)	0.005(1)	0.002(1)
C(6)	8*f*	0.1672(1)	–0.1380(3)	0.4629(1)	0.049(2)	0.056(2)	0.052(2)	0.007(1)	0.014(2)	0.010(1)
C(8)	8*f*	0.2015(1)	–0.1206(3)	0.3157(1)	0.060(2)	0.054(2)	0.044(2)	0.018(2)	0.006(2)	–0.002(2)
C(10)	8*f*	0.2890(1)	0.0721(3)	0.5542(1)	0.059(2)	0.045(2)	0.042(2)	0.013(1)	0.006(2)	0.002(1)
C(11)	8*f*	0.2687(1)	0.0617(3)	0.6079(1)	0.066(2)	0.058(2)	0.046(2)	0.014(2)	0.007(2)	0.002(1)
C(12)	8*f*	0.3020(2)	0.1306(4)	0.6566(1)	0.091(3)	0.064(2)	0.043(2)	0.022(2)	0.005(2)	–0.001(2)
C(13)	8*f*	0.3553(2)	0.2104(4)	0.6525(1)	0.091(3)	0.060(2)	0.054(2)	0.012(2)	–0.008(2)	–0.012(2)
C(14)	8*f*	0.3760(2)	0.2224(4)	0.5997(2)	0.077(2)	0.067(2)	0.067(3)	–0.003(2)	0.000(2)	–0.008(2)
C(15)	8*f*	0.3429(1)	0.1530(4)	0.5509(1)	0.070(2)	0.063(2)	0.048(2)	0.003(2)	0.008(2)	–0.003(2)
C(16)	8*f*	0.0946(2)	–0.2204(6)	0.5238(2)	0.073(2)	0.143(4)	0.068(2)	–0.016(2)	0.028(2)	0.016(2)
C(17)	8*f*	0.0353(1)	–0.2961(4)	0.5156(1)	0.147(5)	0.41(1)	0.143(5)	–0.105(6)	0.069(4)	–0.004(6)
C(18)	8*f*	0.1073(1)	–0.2650(4)	0.3336(1)	0.068(2)	0.058(2)	0.059(2)	0.003(2)	–0.000(2)	–0.003(1)
C(19)	8*f*	0.0533(1)	–0.1498(4)	0.3254(2)	0.064(2)	0.082(2)	0.096(3)	0.000(2)	–0.010(2)	0.009(2)
C(20)	8*f*	0.2990(1)	0.0404(3)	0.3267(1)	0.067(2)	0.055(2)	0.047(2)	0.008(2)	0.018(2)	0.008(1)
C(21)	8*f*	0.3531(1)	–0.0693(4)	0.3235(1)	0.057(2)	0.058(2)	0.039(2)	0.006(2)	0.010(1)	0.007(1)
C(22)	8*f*	0.4085(2)	0.0043(5)	0.3257(2)	0.068(3)	0.066(2)	0.124(3)	–0.002(2)	0.019(2)	0.002(2)
C(23)	8*f*	0.4588(2)	–0.0905(6)	0.3202(2)	0.060(3)	0.097(3)	0.179(5)	0.001(2)	0.026(2)	0.006(3)
C(24)	8*f*	0.4543(2)	–0.2619(6)	0.3133(2)	0.064(3)	0.107(3)	0.109(3)	0.029(2)	0.018(2)	0.008(2)
C(25)	8*f*	0.4001(2)	–0.3382(4)	0.3108(1)	0.084(3)	0.072(2)	0.066(2)	0.022(2)	0.010(2)	0.001(2)
C(26)	8*f*	0.3493(1)	–0.2425(4)	0.3156(1)	0.060(2)	0.062(2)	0.055(2)	0.008(2)	0.008(1)	–0.000(1)

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