Crystal structure of 6-(benz-1*H*-imidazol-2-yl)-2,3-dihydropyridazin-3-one — *N*,*N*-dimethylformamide (1:1), $C_{14}H_{15}N_5O_2$

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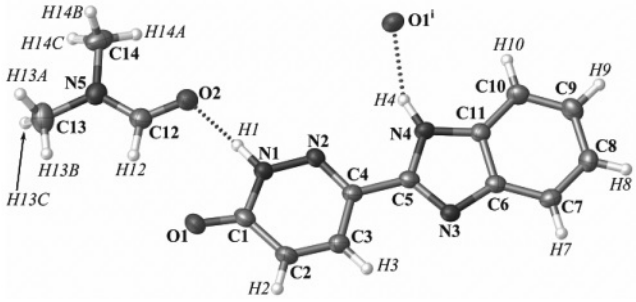

Abstract

$C_{14}H_{15}N_5O_2$, orthorhombic, *Pbca* (no. 61), a = 7.1378(3) Å, b = 12.0046(4) Å, c = 32.1450(13) Å, V = 2754.4 Å^3, Z = 8, $R_{gt}(F)$ = 0.0452, $wR_{ref}(F^2)$ = 0.1009, T = 120 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.02×0.17×0.26 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	7.96 cm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture with Fixed-Chi goniometer, profile data from φ and ω
$2\theta_{max}$:	130.24°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13901, 2352
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1696
$N(param)_{refined}$:	204
Programs:	SAINT, SHELX, OLEX2 [8–10]

Source of material

All solvents and reagents were purchased from *J & K Scientific* company and used without additional purification. 6-Oxo-1,6-dihydropyridazine-3-carboxylic acid was prepared as described in [1]. ^{1}H and ^{13}C{^{1}H}NMR spectra were recorded on a Bruker Avance HD III instrument at 400 and 100 MHz, respectively, in DMSO-d_6 at 378 K, with the solvent resonances used as internal reference standards [δ(^{1}H) = 2.50 p.p.m., δ(^{13}C) = 39.51 p.p.m.]. An equimolar mixture of 6-oxo-1,6-dihydropyridazine-3-carboxylic acid (1.80 g, 12.8 mmol) and *o*-phenylenediamine (1.39 g, 12.8 mmol) were heated in polyphosphorous acid (mass content of P_2O_5 not less thgan 84%; 30 mL) under vigorous stirring at 453 K for 5 h. The resultant black oily slurry was cooled, diluted with water (10 mL) and quenched with a 10% aqueous NaOH solution up to *p*H 8. The precipitated yellow solid was collected by filtration, dried in air and re-crystallized from the minimal amount of hot DMF, that gave 2.52 g of the title compound as a white crystalline solid. Yield 68.7%. A single-crystal suitable for X-ray diffraction analysis was picked up directly from the isolated material. **^{1}H NMR** δ, p.p.m.: 3.06 (very broad s, H_2O and NH); 6.99, 8.17 (both d, both 1H, $^3J_{HH}$ = 9.9 Hz, CH in pyridazinone); 6.35–6.41, 6.48–6.53 (both m, AA'XX' spin system, both 2H, CH in benzene ring). **^{13}C{^{1}H} NMR** δ, p.p.m.: 114.89 (br. s, C^{4,7} in benzimidazole); 122.07 (s, C^{5,6} in benzimidazole); 129.63, 130.71 (both s, CH in pyridazinone); 136.98 (C=N in pyridazinone); 146.92 (N=C–N in in benzimidazole); 159.90 (C=O in pyridazinone). Quaternary signals of C3a,7a in benzimidazole moiety are still broad even at 378 K to be observed.

Experimental details

All C-bonded H atoms were put into calculated positions and refined as riding atoms with a distance C–H = 0.95 Å (CArH) and U_{iso}(H) = 1.2 U_{eq}(C). All N-bonded H atoms were found from difference Fourier synthesis and refined in an isotropic approximation. Noteworthy, the solutions of the title compound exhibit a dynamic behaviour. Thus, all NMR spectal measurements were carried out at elevated temperature in a high-boiling solvent (DMSO-d_6).

Discussion

Pyridazine and pyridazin-3-one moieties are known "pharmacophores" and compounds involving them find considerable use as herbicides and drugs (for some of their pharmaceutical application, see [2, 3]). In the framework of our current studies, the title compound, $C_{11}H_8N_4O{\cdot}C_3H_7NO$, was isolated as the DMF monosolvate. Its asymmetric unit comprises a molecule of 6-(benz-1*H*-imidazol-2-yl)-2,3-dihydropyrazidin-3-one and a DMF molecule. Analysis of the Cambridge Structural Database (CSD; version 5.35, release February 2014 [4]) reveals 23 entries (25 fragments) of structurally characterized substituted 2,3-dihydropyridazin-3-ones which bear only C or H atoms at the 4, 5, and/or 6-positions and 309 entries (434 fragments) for the non-substituted benz-1*H*-imidazol-2-yl moiety. The principal geometrical parameters of the title compound are close to the previously reported ones. The carbonyl oxygen atom O1 only negligibly deviates from the C1/C2/C3/C4/N1/N2 r.m.s. plane [by 0.005(3) Å]. The main molecule in its whole is also nearly planar, with the interplane angle between the r. m. s. planes of the benzimidazole and dihydropyridazinone moieties being only 3.69(7)° [torsion N2/C4/C5/N4 angle equals to 3.8(3)°]. Moreover, the planar DMF molecule is also only slightly twisted respectively to the dihydropyridazinone ring [interplane angle 9.29(7)°]. In crystal structure of the title compound there are two different types of H-bonds, namely, N1–H1···O2 and N4–H4···O1^i {see the Figure; symmetry code: (i) 1–x, ½+y, ½–z; the first order network N_1 = C(8)D; for graph notation, see: [5–7]}. The latter ones are responsible for assembling of the main molecules into zigzag chains along the *b* direction, while the former ones are responsible for the solvent molecule binding. Of interest, the DMF molecule occupies approximately the same effective volume as the benzimidazole moiety that, likely, facilitates the crystal growth (attempts to prepare well-formed crystals from solvents other than DMF were unsuccessful).

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	8*c*	0.456(3)	0.044(2)	0.2900(8)	0.042(7)
H(4)	8*c*	0.398(4)	0.205(2)	0.1724(7)	0.050(8)
H(12)	8*c*	0.443(3)	–0.013(2)	0.3671(6)	0.028(6)
H(2)	8*c*	0.5998	–0.2496	0.2368	0.039
H(3)	8*c*	0.5432	–0.1687	0.1732	0.037
H(7)	8*c*	0.4110	–0.0089	0.0339	0.035
H(8)	8*c*	0.3463	0.1527	–0.0042	0.039
H(9)	8*c*	0.2914	0.3219	0.0293	0.040
H(10)	8*c*	0.3030	0.3360	0.1020	0.037
H(13A)	8*c*	0.4852	0.0644	0.4607	0.067
H(13B)	8*c*	0.4262	–0.0407	0.4330	0.067
H(13C)	8*c*	0.2688	0.0318	0.4559	0.067
H(14A)	8*c*	0.2754	0.2530	0.3857	0.063
H(14B)	8*c*	0.4339	0.2645	0.4207	0.063
H(14C)	8*c*	0.2267	0.2263	0.4333	0.063

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}
C(1)	8*c*	0.5408(3)	–0.1100(2)	0.27262(7)	0.033(1)	0.023(1)	0.033(1)	–0.005(1)	–0.002(1)	0.005(1)
C(2)	8*c*	0.5623(3)	–0.1737(2)	0.23525(7)	0.043(2)	0.019(1)	0.036(1)	0.001(1)	0.000(1)	0.0020(9)
C(3)	8*c*	0.5296(3)	–0.1265(2)	0.19801(7)	0.038(1)	0.024(1)	0.030(1)	–0.002(1)	0.003(1)	–0.002(1)
C(4)	8*c*	0.4744(3)	–0.0125(2)	0.19617(6)	0.031(1)	0.022(1)	0.027(1)	–0.0038(9)	0.001(1)	–0.0011(9)
C(5)	8*c*	0.4376(3)	0.0410(2)	0.15602(6)	0.027(1)	0.020(1)	0.029(1)	–0.0032(9)	0.0017(9)	0.0000(9)
C(6)	8*c*	0.4014(3)	0.0682(2)	0.09068(6)	0.024(1)	0.021(1)	0.029(1)	–0.0018(9)	0.0016(9)	–0.0007(9)
C(7)	8*c*	0.3913(3)	0.0602(2)	0.04764(7)	0.031(1)	0.026(1)	0.031(1)	–0.003(1)	–0.001(1)	–0.0040(9)
C(8)	8*c*	0.3516(3)	0.1560(2)	0.02528(7)	0.036(1)	0.034(1)	0.026(1)	–0.001(1)	–0.005(1)	0.002(1)
C(9)	8*c*	0.3191(3)	0.2578(2)	0.04548(7)	0.036(1)	0.030(1)	0.035(1)	0.006(1)	–0.002(1)	0.006(1)
C(10)	8*c*	0.3263(3)	0.2672(2)	0.08837(7)	0.033(1)	0.024(1)	0.036(1)	0.005(1)	0.000(1)	–0.002(1)
C(11)	8*c*	0.3695(3)	0.1710(2)	0.11042(6)	0.026(1)	0.024(1)	0.027(1)	–0.0033(9)	0.001(1)	–0.0002(9)
C(12)	8*c*	0.4113(3)	0.0678(2)	0.36748(7)	0.038(2)	0.030(1)	0.034(1)	–0.004(1)	0.002(1)	–0.001(1)
C(13)	8*c*	0.3903(4)	0.0346(2)	0.44170(7)	0.040(2)	0.060(2)	0.034(1)	0.003(1)	0.002(1)	0.006(1)
C(14)	8*c*	0.3238(4)	0.2219(2)	0.41178(8)	0.043(2)	0.036(1)	0.047(2)	–0.009(1)	0.009(1)	–0.013(1)
N(1)	8*c*	0.4854(3)	–0.0014(2)	0.26623(6)	0.044(1)	0.0216(9)	0.024(1)	–0.0025(8)	0.0027(9)	–0.0001(8)
N(2)	8*c*	0.4525(3)	0.0488(1)	0.22944(5)	0.034(1)	0.0229(9)	0.025(1)	–0.0026(8)	0.0015(8)	0.0023(8)
N(3)	8*c*	0.4433(3)	–0.0127(1)	0.12011(5)	0.036(1)	0.0207(9)	0.026(1)	–0.0037(8)	0.0022(8)	–0.0009(8)
N(4)	8*c*	0.3931(3)	0.1511(1)	0.15217(6)	0.033(1)	0.0209(9)	0.027(1)	0.0004(8)	0.0025(8)	–0.0035(8)
N(5)	8*c*	0.3762(3)	0.1060(2)	0.40536(6)	0.034(1)	0.035(1)	0.030(1)	–0.0038(9)	0.0021(9)	–0.0021(8)
O(1)	8*c*	0.5651(2)	–0.1440(1)	0.30867(5)	0.052(1)	0.0248(8)	0.0306(9)	–0.0017(8)	–0.0024(8)	0.0055(7)
O(2)	8*c*	0.4046(2)	0.1243(1)	0.33547(5)	0.056(1)	0.0289(8)	0.0307(9)	–0.0034(8)	0.0045(8)	–0.0004(7)

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References

1. Xiong, J.-R.; Xiang, Q.-X.: Synthesis and Mesomorphism of 3,6-Substituted Pyridazines Containing Cholesteryl and Shiff Base. Youji Huaxue **26** (2006) 487–490.
2. Heinisch, G.; Frank, H.: Pharmaceutically Active Pyridazine Derivatives. Part 1. Prog. Med. Chem. **27** (1990) 1–49.
3. Heinisch, G.; Kopelent-Frank, H.: Pharmaceutically Active Pyridazine Derivatives. Part 2. Prog. Med. Chem. **29** (1992) 141–183.
4. Allen, F. H.: The Cambridge Structural Database: a quarter of a million crystal structures and rising. Acta Crystallogr. **B58** (2002) 380–388.
5. Etter, M. C.; MacDonald, J. C.; Bernstein, J.: Graph-Set Analysis of Hydrogen-Bond Patterns in Organic Crystals. Acta Crystallogr. **B46** (1990) 256–262.
6. Bernstein, J.; Davis, R. E.; Shimoni, L.; Chang, N.-L.: Patterns in Hydrogen Bonding: Functionality and Graph Set Analysis in Crystals. Angew. Chem. Int. Ed. Engl. **34** (1995) 1555–1573.
7. Grell, J.; Bernstein, J.; Tinhofer, G.: Graph Set Analysis of Some Hydrogen Bond Patterns. Some Mathematical Concepts. Fakultät für Mathematik und Informatik, Technische Universität München, München 1999.
8. Bruker: APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA (2007).
9. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
10. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. **42** (2009) 339–341.