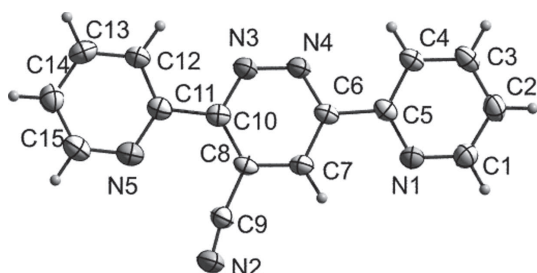


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Crystal structure of 3,6-di-2-pyridinyl-4-pyridazine carbonitrile, $C_{15}H_9N_5$



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Abstract

$C_{15}H_9N_5$, monoclinic, $P2_1/c$ (no. 14), $a = 8.9817(4)$ Å, $b = 11.5791(19)$ Å, $c = 12.065(2)$ Å, $\beta = 102.289(4)^\circ$, $V = 1226.03(3)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0533$, $wR_{\text{ref}}(F^2) = 0.1512$, $T = 173(2)$ K.

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The crystal structure is shown in the figure. Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The ligand was prepared using the method of Butte and Case [4, 5]. 3,6-di(2-pyridyl)tetrazine (1.0 g, 6.8 mmol) and (1.1 g, 20.73 mmol) of acrylonitrile were dissolved in 25 mL of toluene. The resulting mixture was refluxed overnight until the red color of the tetrazine disappeared. The solid residue which remained after removal of the solvent was recrystallized from ethanol to give the title compound as yellow needles. Crystals suitable for X-ray diffraction studies were grown by the solvent diffusion method, where solutions of the compound in dry dichloromethane were layered with a four fold

Table 1: Data collection and handling.

Crystal:	Yellow, rod, size $0.11 \times 0.13 \times 0.14$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	0.90 cm^{-1}
Diffractometer, scan mode:	Bruker Kappa Duo Apex II, φ and ω scans
$2\theta_{\text{max}}$:	56.77°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	9747, 3043
$N(\text{param})_{\text{refined}}$:	181
Programs:	SHELX [1], X-Seed [2], Bruker programs [3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.3805	0.9085	−0.0286	0.050
H(2)	4e	0.3032	0.9258	0.1423	0.050
H(3)	4e	0.3891	0.7906	0.2861	0.047
H(4)	4e	0.5513	0.6418	0.2530	0.042
H(7)	4e	0.6408	0.6412	−0.1053	0.038
H(12)	4e	0.9249	0.2542	0.1706	0.049
H(13)	4e	1.0813	0.0965	0.1560	0.060
H(14)	4e	1.1704	0.0703	−0.0118	0.053
H(15)	4e	1.0974	0.2009	−0.1582	0.052

excess of hexane and allowed to stand undisturbed in the dark at ambient temperature for 2 days.

Experimental details

All hydrogen atoms were placed in idealised positions and refined in riding models with U_{iso} assigned the values of 1.2 times those of their parent atoms and the distances of C–H were constrained to 0.95 Å for all the aromatic hydrogens.

Discussion

Pyridazines are heterocyclic compounds with an aromatic ring system containing two adjacent nitrogen atoms. These nitrogen atoms offer a unique chemistry as the nitrogen atoms interact with suitable substrates with acidic functionalities to generate novel supramolecular assemblies with exotic structures [6–9]. They also act as building blocks in several

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Table 3: Fractional atomic coordinate and displacement parameters (Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
N(1)	4e	0.5055(2)	0.7679(1)	0.0078(1)	0.0393(9)	0.0412(9)	0.0291(8)	0.0050(7)	0.0061(7)	−0.0003(6)
N(2)	4e	0.7960(2)	0.4876(2)	−0.2766(1)	0.068(1)	0.052(1)	0.0323(9)	0.0076(9)	0.0201(9)	0.0039(8)
N(3)	4e	0.7971(2)	0.4361(1)	0.1249(1)	0.044(1)	0.0385(9)	0.0271(8)	0.0029(7)	0.0100(7)	0.0001(6)
N(4)	4e	0.7095(2)	0.5236(1)	0.1452(1)	0.0419(9)	0.0368(8)	0.0262(8)	0.0011(7)	0.0113(7)	0.0013(6)
N(5)	4e	0.9748(2)	0.3041(1)	−0.0821(1)	0.044(1)	0.044(1)	0.0337(9)	−0.0018(8)	0.0112(7)	0.0021(7)
C(1)	4e	0.4149(2)	0.8530(2)	0.0291(2)	0.044(1)	0.045(1)	0.036(1)	0.0094(9)	0.0053(9)	−0.0004(9)
C(2)	4e	0.3685(2)	0.8644(2)	0.1310(2)	0.039(1)	0.048(1)	0.037(1)	0.0075(9)	0.0061(8)	−0.0108(9)
C(3)	4e	0.4191(2)	0.7851(2)	0.2154(2)	0.038(1)	0.050(1)	0.031(1)	−0.0022(9)	0.0110(8)	−0.0110(8)
C(4)	4e	0.5142(2)	0.6973(2)	0.1958(2)	0.039(1)	0.040(1)	0.0272(9)	−0.0009(8)	0.0092(8)	−0.0024(7)
C(5)	4e	0.5546(2)	0.6914(2)	0.0909(1)	0.0291(9)	0.0329(9)	0.0271(9)	−0.0053(7)	0.0065(7)	−0.0064(7)
C(6)	4e	0.6524(2)	0.5974(2)	0.0628(1)	0.030(1)	0.0340(9)	0.0232(8)	−0.0058(7)	0.0067(7)	−0.0021(7)
C(7)	4e	0.6809(2)	0.5871(2)	−0.0475(1)	0.037(1)	0.0337(9)	0.0244(8)	−0.0020(8)	0.0081(7)	0.0000(7)
C(8)	4e	0.7703(2)	0.4944(1)	−0.0683(1)	0.0301(9)	0.0324(9)	0.0247(8)	−0.0084(7)	0.0080(7)	−0.0020(7)
C(9)	4e	0.7925(2)	0.4834(2)	−0.1824(2)	0.041(1)	0.034(1)	0.0316(9)	−0.0005(8)	0.0124(8)	−0.0001(7)
C(10)	4e	0.8286(2)	0.4190(2)	0.0218(1)	0.030(1)	0.0302(9)	0.0289(9)	−0.0058(7)	0.0053(7)	−0.0007(7)
C(11)	4e	0.9257(2)	0.3175(1)	0.0142(1)	0.033(1)	0.0301(9)	0.0284(9)	−0.0068(7)	0.0055(7)	−0.0044(7)
C(12)	4e	0.9624(2)	0.2422(2)	0.1036(2)	0.047(1)	0.049(1)	0.0274(9)	0.0089(9)	0.0103(9)	0.0014(8)
C(13)	4e	1.0541(3)	0.1494(2)	0.0949(2)	0.059(2)	0.053(1)	0.038(1)	0.012(1)	0.009(1)	0.0141(9)
C(14)	4e	1.1063(2)	0.1337(2)	−0.0038(2)	0.046(1)	0.039(1)	0.049(1)	0.0057(9)	0.013(1)	−0.0037(9)
C(15)	4e	1.0631(2)	0.2122(2)	−0.0897(2)	0.045(1)	0.052(1)	0.036(1)	−0.003(1)	0.0148(9)	−0.0043(9)

bioinorganic compounds and as ligands in the preparation of novel coordination complexes [7, 10]. Pyridazines are also known to exhibit versatile biological activities. The 3,6-di(2-pyridyl)pyridazines represent one of the most interesting ligand systems among the pyridazines. These compounds can act as metal coordinating ligands for copper, silver and nickel ions resulting in grid-like metal complexes [11, 12]. In addition, many binuclear metal complexes of these ligands with nickel, copper and platinum have been reported [4, 13].

Highly functionalized pyridazine are easily accessible via an inverse Diels-Alder reaction between the 1, 2, 4, 5-tetrazine and a wide variety of acetylenes, whereby the tetrazine acts as the electron deficient diene [4, 14]. The synthesis of 3,6-di(2-pyridyl)tetrazine and its utilization in inverse-type Diels-Alder reactions was first described by Butte and Case [5]. In continuation of that work other groups have reported similar cycloadditions to the 3,6-di(2-pyridyl)tetrazine, resulting in monosubstituted octyl, carboxy ethyl or tetrahydropyranlyl diethyl ethers of methanol, hexanol and fullerenes [4, 15, 16].

The title compound was first reported by Butte and Case [7] but its crystal structure has not been elucidated until now. It crystallizes with one molecule in the asymmetric unit. The N4–N3 bond length is 1.337(2) Å, C5–N1 = 1.341(2) Å and C11–N5 = 1.336(2) Å and these are comparable to the bond lengths of similar reported molecules [10, 17]. The dihedral angles between the planes defined by N1, C1–C5 and N5, C11–C15 are of 5.47 (0.11)° and 6.96 (0.11)° showing that the planes are coplanar.

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