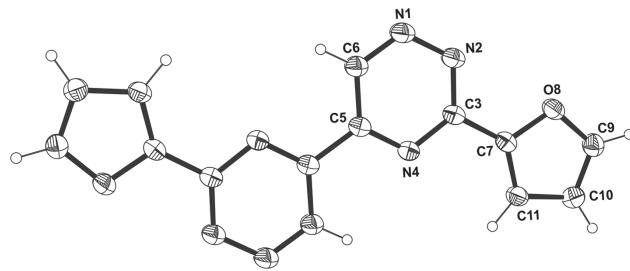


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Crystal structure of 3,3'-di(furan-2-yl)-5,5'-bi-1,2,4-triazine



DOI 10.1515/ncrs-2016-0103

Received April 4, 2016; accepted September 20, 2016; available online October 10, 2016

Abstract

$C_{14}H_8N_6O_2$, monoclinic, $P2_1/c$ (no. 14), $a = 9.2129(18)$ Å, $b = 5.0321(10)$ Å, $c = 13.760(3)$ Å, $\beta = 100.02(3)^\circ$, $V = 628.2(2)$ Å 3 , $Z = 2$, $R_{\text{gt}}(F) = 0.0416$, $wR_{\text{ref}}(F^2) = 0.1115$, $T = 296$ K.

CCDC no.: 1504851

Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was prepared by the following method: to the round bottom flask were added 3,3'-dichloro-5,5'-bi-1,2,4-triazine (0.46 g, 2 mmol) in anhydrous dioxane 15 mL and 2-tri(*n*-butylstannyl)furan (2.52 mL, 8.0 mmol) and Pd(PPh₃)₄ (0.23 g, 10 mol%). The reaction mixture was refluxed for 24 h. The solvent was evaporated and the precipitate was filtered. The filtrate was dissolved in ethyl acetate and washed in

Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	0.40 × 0.20 × 0.10 mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ :	9.3 cm $^{-1}$
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{\text{max}}$, completeness:	125.8°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7875, 1064, 0.051
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 911
$N(\text{param})_{\text{refined}}$:	101
Programs:	Bruker programs [6], SHELX [7], WinGX [8]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^* / U_{\text{eq}}$
O8	0.11665(12)	0.1992(2)	0.45906(9)	0.0501(4)
N1	0.33882(18)	0.7470(3)	0.65107(11)	0.0586(5)
N2	0.26521(16)	0.5666(3)	0.58855(10)	0.0527(4)
N4	0.37985(13)	0.7308(3)	0.45753(9)	0.0399(4)
C3	0.28753(16)	0.5666(3)	0.49564(11)	0.0400(4)
C5	0.44880(16)	0.9072(3)	0.51916(11)	0.0390(4)
C6	0.42757(19)	0.9162(4)	0.61733(12)	0.0505(5)
H6	0.4769	1.0437	0.6596	0.076*
C7	0.21164(16)	0.3753(3)	0.42705(12)	0.0409(4)
C9	0.06534(19)	0.0412(4)	0.38049(13)	0.0505(5)
H9	–0.0019	–0.0962	0.3814	0.076*
C10	0.12417(18)	0.1091(3)	0.30168(12)	0.0487(5)
H10	0.1066	0.0291	0.2398	0.073*
C11	0.21847(18)	0.3269(3)	0.33141(12)	0.0460(5)
H11	0.2745	0.4191	0.2925	0.069*

portions with brine. The organic layer was evaporated and purified by column chromatography using dichloromethane. Crystallisation from ethyl acetate/hexane gives a yellow solid as main product and 3-chloro-3'-(furan-2-yl)-5,5'-bi-1,2,4-triazine as side product. 0.46 g; Yield 79%, mp. 269–270 °C. **IR** (KBr) cm $^{-1}$: 3145(CH₃), 1531–1584, 1094 (C—O—C). **¹H NMR** (400 MHz, CDCl₃): δ 9.69 (s, 1H, CH), 7.85 (d, $J = 3.6$ Hz, 1H, CH), 7.68 (d, $J = 1.6$ Hz, 1H, CH), 6.62 (dd, $J_1 = 1.6$ Hz, $J_2 = 3.6$ Hz, 1H, CH). **¹³C NMR** (100 MHz, CDCl₃): δ 155.99, 154.19, 153.11, 144.48, 142.81, 128.24, 120.00. **Elemental**

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analysis for C₁₄H₈N₆O₂ calcd.: C: 57.50; H: 2.70; N: 28.80. Found: C: 57.45; H: 2.68; N: 28.70. Crystals suitable for X-ray structure analysis were grown by slow evaporation of a chloroform solution.

Experimental details

All hydrogen atoms were identified in difference Fourier syntheses and treated as riding on their parent C atoms with C—H distances of 0.93 Å (aromatic) and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ in the refinement procedure.

Discussion

Nitrogen-containing heterocycles are extensively used as bridging ligands in coordination and supramolecular chemistry. Heterocyclic compounds containing soft donor atoms are capable of separating two groups of elements. For example, it has been reported that ligands containing aromatic N atoms as donor atoms coordinate An(III) more strongly than Ln(III), due to a greater covalent character of the An(III)—N bond [1–3]. As a continuation of our structural study on 6,6'-bis(substituted)-5,5'-bi-1,2,4-triazines as potential N-heterocyclic ligands for the extraction of nuclear waste [4], we describe in this paper the crystal structure of 3,3'-di(furan-2-yl)-5,5'-bi-1,2,4-triazine.

The two 3-(furan-2-yl)-1,2,4-triazine parts of the title molecule are connected by the Csp²—Csp² single bond of 1.488(3) Å. The two parts are related by a crystallographic center of symmetry and consequently they possess *trans* conformation. The furan and 1,2,4-triazine rings are planar to within 0.0033(18) and 0.0091(15) Å, respectively, and they are almost coplanar confirmed by the torsion angle N4—C3—C7—O8 of 179.51(12)°. The molecule is planar as a whole, which is characteristic for π -conjugated organic systems. The consequence of this conjugation is occurrence of strong intramolecular interaction N2···O8 with the distance between N2 and O8 atoms of 2.7600(19) Å significantly shorter than the sum of the van der Waals radii of nitrogen and oxygen (3.07 Å). Similar effect is observed e.g. in 2,2'-bi(3,4-ethylenedioxythiophene) π -conjugated system [5]. There are no intermolecular hydrogen bonds in the crystal structure of

the title compound. The molecular packing is determined by van der Waals interactions. Moreover, the pairs of the furan and 1,2,4-triazine rings belonging to the translation-related molecules in [010] direction show a centroid-to-centroid separation of 3.6825(12) Å and the angle between the overlapping planes of these rings of 1.99(9)°. The π — π distances of 3.2241(7) and 3.2715(6) Å between furan ring at (x, y, z) and triazine ring at (x, -1+y, z) and triazine ring at (x, y, z) and furan ring at (x, 1+y, z), respectively, are close to van der Waals distance of about 3.4 Å for the overlapping π -aromatic ring systems.

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