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The crystal structure of 10-(3,5-di(pyridin-4-yl)phenyl)-10*H*-phenoxazine dihydrate, C₂₈H₂₃N₃O₃

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Abstract

C₂₈H₂₃N₃O₃, orthorhombic, *Pna*2₁ (no. 33), *a* = 29.0466(11) Å, *b* = 5.2448(3) Å, *c* = 14.4825(7) Å, *V* = 2206.32(19) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0511, *wR*_{ref}(*F*²) = 0.1341, *T* = 100.00(10) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.11 × 0.10 × 0.09 mm
Wavelength:	Cu Kα radiation (1.54184 Å)
μ:	0.72 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
θ _{max} , completeness:	73.6°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	5115, 3451, 0.044
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 3078
<i>N</i> (<i>param</i>) _{refined} :	313
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4]

Source of material

In a representative experiment 3,5-di(pyridin-4-yl)aniline (2.0 mmol) reacted with CuBr₂ (2.1 mmol) in a HBr (20 mL) solution at 50 °C to give 4,4'-(5-bromo-1,3-phenylene) dipyridine. This intermediate (1 mmol) was added to a methanolic solution (30 mL) containing 10*H*-phenoxazine (1.2 mmol). The reaction mixture was refluxed for 12 h at 120 °C under the catalysis of NaOBu-*t* and Pd(OAc)₂. The precipitated residue was removed from the solution by filtration and then washed with methanol and chloroform. Crystals were obtained by slow evaporation of mixed solution of methanol and chloroform (3:1, v/v) at room temperature after a week.

Experimental details

The title compound was collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. The data were collected and processed using CrysAlisPro [1]. The structures were solved by direct methods using Olex2 software [2], and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018 [3] using a full-matrix least squares procedure based on *F*². The weighted *R* factor, *wR* and goodness-of-fit *S* values were obtained based on *F*². H atoms attached to C were included in calculated positions and refined as riding atoms, with *d* (N–H) = 0.86 Å, *d* (C–H) = 0.93 Å (aromatic). Their *U*_{iso} values were set to 1.2*U*_{eq} of the parent atoms. Water molecules were refined as rigid groups and *HU*_{iso} was set to 1.5*U*_{eq} of the parent atom.

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
O1	0.58161 (9)	0.8391 (6)	0.5421 (2)	0.0268 (7)
O2	0.26731 (12)	−0.2047 (7)	0.1738 (2)	0.0383 (8)
H2A	0.275046	−0.191031	0.230170	0.057*
H2B	0.272958	−0.359325	0.160309	0.057*
O3	0.28471 (12)	0.2850 (7)	0.0964 (2)	0.0344 (8)
H3A	0.291289	0.270316	0.039454	0.052*
H3B	0.279445	0.133392	0.114213	0.052*
N1	0.48623 (11)	0.7683 (7)	0.5591 (2)	0.0227 (7)
N2	0.30080 (11)	0.0061 (7)	0.3443 (3)	0.0259 (8)
N3	0.31019 (12)	1.1718 (7)	0.9043 (3)	0.0269 (8)
C1	0.50318 (13)	0.9385 (7)	0.4933 (3)	0.0195 (8)
C2	0.47539 (14)	1.0774 (8)	0.4340 (3)	0.0235 (8)
H2	0.443760	1.049877	0.434301	0.028*
C3	0.49392 (15)	1.2570 (8)	0.3740 (3)	0.0268 (9)
H3	0.474747	1.347766	0.334395	0.032*
C4	0.54122 (15)	1.3010 (9)	0.3731 (3)	0.0299 (10)
H4	0.553666	1.425657	0.334859	0.036*
C5	0.56957 (14)	1.1569 (8)	0.4299 (3)	0.0264 (9)
H5	0.601249	1.182078	0.428349	0.032*
C6	0.55133 (13)	0.9784 (8)	0.4880 (3)	0.0224 (8)
C7	0.56438 (13)	0.6440 (8)	0.5951 (3)	0.0239 (9)
C8	0.59565 (14)	0.4858 (9)	0.6381 (3)	0.0279 (9)
H8	0.627054	0.512273	0.630061	0.033*
C9	0.58026 (16)	0.2865 (9)	0.6937 (3)	0.0318 (10)
H9	0.601301	0.182314	0.724022	0.038*
C10	0.53346 (15)	0.2442 (8)	0.7035 (3)	0.0287 (10)
H10	0.522987	0.109779	0.739760	0.034*
C11	0.50210 (14)	0.4030 (8)	0.6591 (3)	0.0255 (9)
H11	0.470722	0.373516	0.666089	0.031*
C12	0.51680 (13)	0.6035 (8)	0.6047 (3)	0.0203 (8)
C13	0.43737 (12)	0.7376 (8)	0.5723 (3)	0.0208 (8)
C14	0.41241 (13)	0.5878 (8)	0.5121 (3)	0.0213 (8)
H14	0.426636	0.519247	0.460174	0.026*
C15	0.36546 (13)	0.5383 (8)	0.5288 (3)	0.0229 (8)
C16	0.34472 (13)	0.6503 (8)	0.6048 (3)	0.0212 (8)
H16	0.313789	0.617748	0.616458	0.025*
C17	0.36885 (12)	0.8097 (7)	0.6640 (3)	0.0202 (8)
C18	0.41629 (13)	0.8506 (8)	0.6477 (3)	0.0218 (8)
H18	0.433290	0.952973	0.687576	0.026*
C19	0.34707 (13)	0.9408 (8)	0.7437 (3)	0.0203 (8)
C20	0.30840 (14)	0.8407 (9)	0.7885 (3)	0.0254 (9)
H20	0.294038	0.694480	0.766340	0.030*
C21	0.29182 (14)	0.9641 (9)	0.8670 (3)	0.0295 (10)
H21	0.265889	0.895716	0.895360	0.035*
C22	0.34666 (13)	1.2712 (8)	0.8591 (3)	0.0259 (9)
H22	0.360098	1.418588	0.882530	0.031*
C23	0.36508 (13)	1.1655 (8)	0.7799 (3)	0.0244 (9)
H23	0.389666	1.245055	0.750489	0.029*
C24	0.34144 (13)	0.3636 (8)	0.4644 (3)	0.0207 (8)
C25	0.35050 (14)	0.3649 (9)	0.3708 (3)	0.0255 (9)
H25	0.370579	0.485126	0.346114	0.031*
C26	0.32970 (14)	0.1873 (9)	0.3136 (3)	0.0283 (9)
H26	0.336064	0.193846	0.250746	0.034*
C27	0.31010 (12)	0.1817 (8)	0.4969 (3)	0.0220 (8)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H27	0.301778	0.177885	0.558921	0.026*
C28	0.29166 (13)	0.0071 (9)	0.4352 (3)	0.0255 (9)
H28	0.271778	−0.116607	0.458098	0.031*

Comment

Phenoxazine derivatives have been identified in various biological systems including pigments and antibiotics [4–6] and extensively investigated in the past few decades because of their vast applications such as antimicrobial effects [7, 8], organic dyes [9], anti-cancer effects [10, 11] and pharmaceutical intermediates [12]. In particular, metal-free organic dyes with a core phenoxazine chromophore represent a rapidly growing field of research [13–15]. Here we report the crystal structure of a new phenoxazine derivative to expect a better understanding of this structure.

The asymmetric unit of the title structure contains one 10-(3,5-di(pyridin-4-yl)phenyl)-10*H*-phenoxazine and two water molecules. From the molecular structure, it can be calculated that the dihedral angle between the phenoxazine ring(C(1)–C(12)) and the benzene ring (C(13)–C(18)) is 82.582°, which indicates that the two rings are not coplanar. In addition, the torsion angle of C14–C13–N1–C6 (110.1°) and C17–C17–C19–C23(−22.9°) can illustrate non-planar property of the molecule. Interestingly the title compound appears to be polymorphic. The structure of a monoclinic, monohydrate form will be the subject of a future publication. All water H atoms are involved in hydrogen bonding; D···A distances are in the 2.848(5)–2.946(5) Å range and D–H···A angles in the 153.8–172.2° range. In addition, several other contacts are formed, for instance C16–H16c···O3 and C27–H27···O2 with d(C···O) distance of 3.007 and 2.697 Å, respectively. The distance between the adjacent phenoxazine rings of C(1)–C(12) is 3.422 Å, pointing towards the presence of face-to-face π–π stacking. Other geometric parameters are in expected ranges [16]. To the best of our knowledge, the present structure has not been reported in the literature. The structure of a parent compound has been published earlier [17].

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