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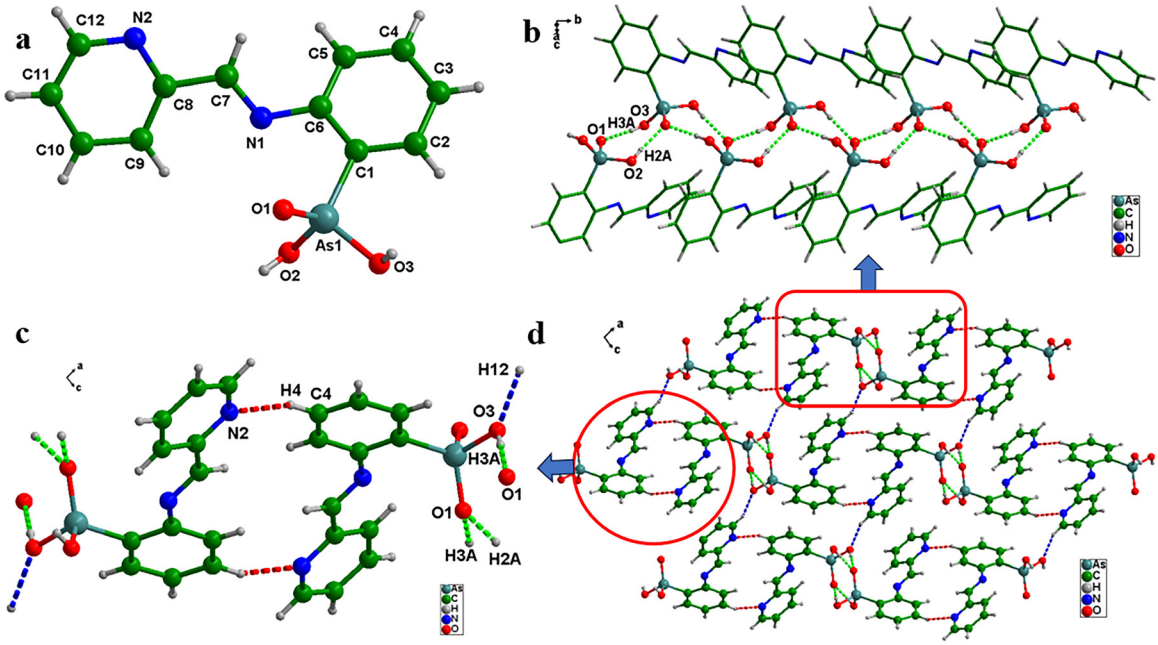
The crystal structure of (*E*)-(2-((pyridin-2-ylmethylene)amino)phenyl)arsonic acid, $C_{12}H_{11}AsN_2O_3$



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Abstract

$C_{12}H_{11}AsN_2O_3$, monoclinic, $P2_1/c$ (no. 14), a = 10.1258(10) Å, b = 6.3254(5) Å, c = 19.1102(16) Å, β = 97.578(3)°, V = 1213.31(18) Å^3, Z = 4, $R_{gt}(F)$ = 0.0409, $wR_{ref}(F^2)$ = 0.1027, T = 150.0 K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

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Table 1: Data collection and handling.

Crystal:	Colourless needle
Size:	0.22 × 0.15 × 0.11 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	2.80 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω scans
θ_{max}, completeness:	26.4°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12667, 2488, 0.084
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1834
$N(param)_{refined}$:	169
Programs:	Bruker,[1] Olex2,[2] SHELX[3,4]

1 Source of materials

A solution containing 5.34 g (20 mmol) of 2-aminophenylarsonic acid and 3.04 g (20 mmol) of o-vanillin in 100 mL ethanol was catalytically stirred with 1 drop of concentrated HCl at 333 K for 2 h. Colourless precipitates formed during the reaction were collected by filtration, followed by vacuum drying. The title compound was purified

via recrystallization from ethanol. Subsequent slow evaporation of the filtrate in air afforded colourless crystals. Yield: 65.8 % (calculated relative to 2-aminophenylarsonic acid).

2 Experimental details

The structure was solved by Direct Methods with the SHELXS-2018 program. All H-atoms from C were positioned with idealized geometry and refined isotropically (U_{iso}(H) = 1.2U_{eq}(C)) using a riding model with C–H = 0.950 Å. The H-atoms from O atoms were positioned with Q peaks and refined isotropically with U_{iso}(H) = 1.5U_{eq}(O) and O–H = 0.771 and 0.776 Å freely.

3 Comment

Many single-crystal structures based on 2-aminophenylarsonic acid have been systematically reported, including organic molecules[5,6] and organic salts.[7,8] 2-Aminophenylarsonic acid also serves as organic ligand for constructing metal complexes with many transition metal ions, including Cu^{2+},[9] Co^{3+},[10] and Sn^{4+}[11,12] etc., as well as polyoxometalate clusters. The latter includes polyoxovanadates,[13] polyoxomolybdates,[14,15] and polyoxotungstates.[16,17] Notably, its derivatives modified at the 2-amino position exhibit significant value in organic synthetic chemistry[18–20] and coordination chemistry: some derivatives serve as organic ligands for constructing metal complexes with Zn^{2+}[21] and Cd^{2+} cations.[22] One of the most efficient strategies for modifying 2-aminophenylarsonic acid is the Schiff base reaction, which leverages the diversity of aromatic aldehydes to achieve structural tunability. In 2015, Percino et al. first reported the synthesis and single-crystal structure of a Schiff base ligand formed by the equimolar reaction of 2-aminophenylarsonic acid with salicylaldehyde in ethanol, using HCl as a catalyst.[23] In 2019, they further expanded this work by characterizing three (E)-(2-(substituted benzylidene)aminophenyl)arsonic acids.[24] We just focused on the structural elucidation of a novel Schiff base arsonic acid ligand: E-(2-(2-hydroxy-3-methoxybenzylidene)aminophenyl) arsonic acid,[25] which was synthesized through the condensation of 2-aminophenylarsonic acid with 2-hydroxy-3-methoxybenzaldehyde. The successful determination of these crystal structures of Schiff base arsonic acids provide critical insights into the spatial configuration of such ligands. We herein firstly report one N-heterocyclic modified Schiff base arsonic acid: the title compound, (*E*)-(2-((pyridin-2-ylmethylene)amino)phenyl)arsonic acid.

The title compound, named (*E*)-(2-((pyridin-2-ylmethylene) amino)phenyl)arsonic acid, with the molecular formula $C_{12}H_{11}AsN_2O_3$, crystallizes in monoclinically, $P2_1/c$ (no. 14). As shown in the figure (a), the asymmetrical unit is made of one whole (*E*)-(2-((pyridin-2-ylmethylene)amino)phenyl)arsonic acid. The As(V) atom adapts a tetrahedral configuration, with the four bond lengths of As–C and As–O are 1.893, 1.656, 1.701 and 1.711 Å, respectively, which are compatible with the reported results.[23–25] The phenyl and pyridinyl are nearly plane. Two (*E*)-(2-((pyridin-2-ylmethylene)amino)phenyl)arsonic acid molecules are linked by non-classical hydrogen bonds C4–H4···N2 to build a dimer (see figure (c)). In figure (b), one-dimensional chains are formed by the strong intermolecular hydrogen bonds O2–H2A···O1 and O3–H3A···O1 (both the two distances of the donor···aceptor are 2.598 Å, and the angle is almost straight: the one is 174.10°, and the other is 177.58°). A sheet structure is generated combining the dimers and the chains. Finally, the sheets finally build a three dimensional supramolecular structure through the non-classical hydrogen bond C12–H12···O3 (figure (d)).

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