

4-[(2-Hydroxyethyl)iminomethyl]-5-hydroxymethyl-2-methylpyridin-3-ol

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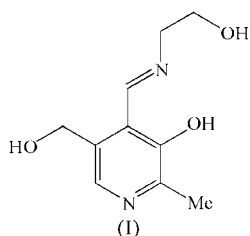
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The title compound, $C_{10}H_{14}N_2O_3$, is a Schiff base which is derived from pyridoxal and represents, therefore, a vitamin B₆-related compound. Molecules are linked into sheets by a combination of O—H···O and O—H···N hydrogen bonds.

Comment

Vitamin B₆ is an essential cofactor to a large number of enzymes that catalyse many reactions of amino acids (Sykes *et al.*, 1991). One of the active forms of vitamin B₆ is the heterocyclic aldehyde pyridoxal. Much attention has been focused on the coordination chemistry of pyridoxal Schiff bases with amino acids (Christensen, 1957; Long *et al.*, 1980; Dawes *et al.*, 1982; Walz *et al.*, 1983; Rao *et al.*, 1985; Astheimer *et al.*, 1985; Sykes *et al.*, 1991; Costa Pessoa *et al.*, 1999). No X-ray structure of a free pyridoxal Schiff base has been reported to date, since the Schiff base ligand is usually generated in the coordination sphere of the transition metal. This approach is impractical for complexation with moisture-sensitive reagents, for instance, halogenosilanes or organometallic derivatives. The title compound, (I), was prepared in order to supply an alternative ligand system for the preparation of vitamin B₆-Schiff base complexes. Fig. 1 shows the molecular structure of (I) and the atomic labelling scheme. Selected bond lengths are listed in Table 1.



The substituted pyridine ring has bond lengths that differ somewhat from those expected for an unsubstituted pyridine ring owing to the irregular substitution pattern of the pyridoxal ring. The enamine group (N2=C7) has a bond length of 1.280 (1) Å, which is typical for this type of Schiff base (Böhme & Günther, 2006, 2007; Böhme *et al.*, 2006). The

hydroxymethyl group is nearly coplanar with the pyridine ring, with a C3—C4—C8—O2 torsion angle of 176.28 (8)°. The same holds for the enamine group, with a C2—C3—C7—N2 torsion angle of 0.9 (1)°. Atom N2 is bonded to the O1—H1 group *via* a hydrogen bridge (Table 2), forming an intramolecular six-membered pseudo-ring. The 2-hydroxyethyl

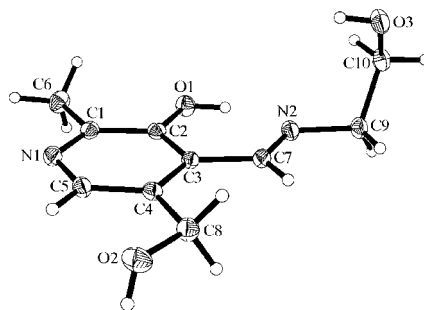


Figure 1
The molecular structure of (I), drawn with 50% probability displacement ellipsoids.

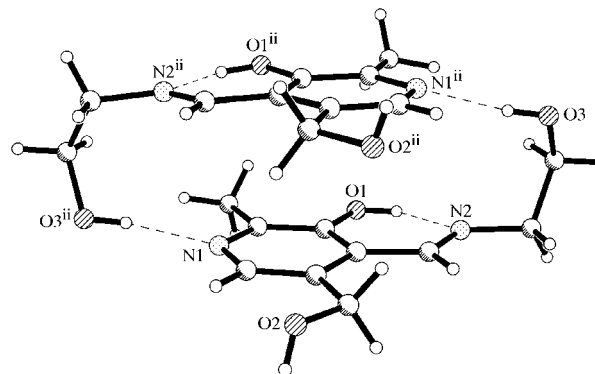


Figure 2
Head-to-tail dimers of (I), formed by O3—H3···N1A hydrogen bonds and π - π interactions. [Symmetry code: (ii) $-x + 1, y, -z + \frac{1}{2}$]

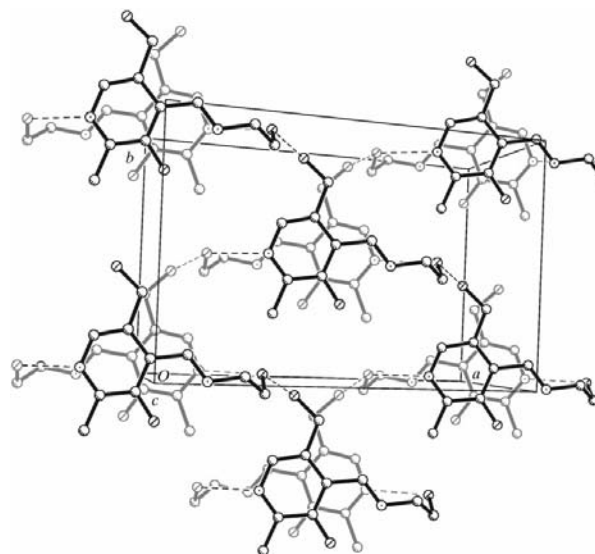


Figure 3
The packing of (I) in the *c* direction, showing the sheet structure which is built up by intermolecular hydrogen bridges between the dimers. (The lower part of the hydrogen-bridged dimers is shown shaded and H atoms have been omitted for clarity.)

group (C9/C10/O3) is rotated out of the molecular plane, with an N2—C9—C10—O3 torsion angle of 74.5 (1)°. The O3—H3 group forms a hydrogen bridge with the pyridine N atom of another molecule, giving pairs of molecules which are connected 'head-to-tail' (see Fig. 2). These pairs are further stabilized by π – π interactions between π -conjugated units, with a distance of 3.030 Å between the planes formed by atoms N1, C1–C8, N2 and O1. The crystal packing is further stabilized by O—H...O hydrogen bonds, which generate a sheet structure parallel to the crystallographic *ab* plane (Fig. 3).

Compound (I) represents a potentially useful ligand for the preparation of complexes with main group and transition metals. Furthermore, the preparation of coordination polymers seems to be feasible because of the presence of three OH groups and two nitrogen-donor positions in the molecule.

Experimental

Pyridoxal hydrochloride (4.07 g, 20 mmol) and sodium methanolate (1.08 g, 20 mmol) were mixed in ethanol (200 ml). The suspension was stirred at room temperature and treated with 2-aminoethanol (1.22 g, 1.2 ml, 20 mmol). The reaction mixture was boiled at reflux temperature for 2 h. After that time, a yellow solution and a white precipitate were formed. The precipitate (NaCl) was filtered off and washed with ethanol. The filtrate was reduced in a vacuum to 50 ml. The product was precipitated by adding *n*-hexane (30 ml) and was isolated by filtration (yield 3.6 g, 85.6%; m.p. 421 K). NMR (DMSO-*d*₆, 298 K, TMS): ¹H δ 2.37 (*s*, Me, H6), 3.70, 3.72 (2 × *t*, CH₂, H9, H10), 4.64 (*s*, CH₂, H8), 4.87 (*s* broad, O3—H3), 5.37 (*s* broad, O2—H2), 7.86 (*s*, C5—H5), 8.86 (*s*, N=C7—H7), 14.49 (*s* broad, O1—H1); ¹³C δ 18.9 (C6), 58.5, 60.5, 60.9 (C8, C9, C10), 118.9, 132.9, 136.9, 148.8, 155.2 (C1—C5), 164.5 (C7).

Crystal data

C ₁₀ H ₁₄ N ₂ O ₃	<i>V</i> = 1955.99 (10) Å ³
<i>M_r</i> = 210.23	<i>Z</i> = 8
Monoclinic, <i>C</i> 2/ <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 16.2739 (5) Å	<i>μ</i> = 0.11 mm ^{−1}
<i>b</i> = 9.6403 (3) Å	<i>T</i> = 153 (2) K
<i>c</i> = 13.5513 (4) Å	0.60 × 0.16 × 0.10 mm
<i>β</i> = 113.069 (2)°	

Data collection

Bruker SMART CCD area-detector diffractometer	16737 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2858 independent reflections
<i>T</i> _{min} = 0.935, <i>T</i> _{max} = 0.989	2292 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.029

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.038	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> (<i>F</i> ²) = 0.109	
<i>S</i> = 1.05	Δ <i>ρ</i> _{max} = 0.46 e Å ^{−3}
2858 reflections	Δ <i>ρ</i> _{min} = −0.20 e Å ^{−3}
140 parameters	

There are few structure reports of Schiff bases with oxygen in the *ortho* position where the intramolecular bridging H atom is localized at the N atom (*e.g.* Pradeep, 2005; Dubs *et al.*, 2000; Hopfl *et al.*, 1998). Therefore, atom H1 was located by difference Fourier synthesis and refined without constraints. All other H atoms were placed in geometrically idealized positions and treated as riding atoms, with C—H = 0.95–0.99 Å and O—H = 0.84 Å. For all H atoms, *U*_{iso}(H) =

Table 1
Selected bond lengths (Å).

N1—C1	1.330 (1)	C1—C6	1.497 (1)
N1—C5	1.355 (1)	C2—C3	1.404 (1)
N2—C7	1.280 (1)	C3—C4	1.410 (1)
N2—C9	1.456 (1)	C3—C7	1.466 (1)
O1—C2	1.343 (1)	C4—C5	1.381 (1)
O2—C8	1.414 (1)	C4—C8	1.516 (1)
O3—C10	1.427 (1)	C9—C10	1.520 (2)
C1—C2	1.413 (1)		

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...N2	0.885 (17)	1.765 (16)	2.573 (1)	150.7 (15)
O2—H2...O3 ⁱ	0.84	1.98	2.817 (1)	173
O3—H3...N1 ⁱⁱ	0.84	1.94	2.775 (1)	172

Symmetry codes: (i) *x* + ½, *y* + ½, *z*; (ii) *−x* + 1, *y*, *−z* + ½.

*kU*_{eq}(carrier), where *k* = 1.5 for methyl and hydroxy groups, and *k* = 1.2 for all other H atoms.

Data collection: SMART (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP in SHELXTL-Plus (Sheldrick, 1991); software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3146). Services for accessing these data are described at the back of the journal.

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