

Intramolecular hydrogen transfer in
(S)-2-[(1-benzyl-2-hydroxyethylimino)methyl]-
4-nitrophenol, a new chiral Schiff base

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Key indicators

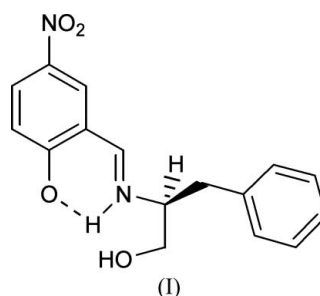
Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.041
 wR factor = 0.108
Data-to-parameter ratio = 7.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The synthesis and crystal structure of the new title chiral Schiff base, $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4$, derived from the condensation of L-phenylalaninol [(S)-(-)-2-amino-3-phenyl-1-propanol] and 5-nitrosalicylaldehyde (2-hydroxy-5-nitrobenzaldehyde), are presented. There are two molecules in the asymmetric unit and they are stabilized in the solid state in the NH tautomeric form.

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Comment

Intramolecular hydrogen transfer from the *o*-hydroxy group to the imine-N atom is of prime importance with respect to the solvato-, thermo- and photochromic properties exhibited by *o*-hydroxy Schiff bases (Filarowski, 2005; Hadjoudis *et al.*, 2004). Such proton-exchanging materials can be utilized for the design of various molecular electronic devices (Alarcón *et al.*, 1999). On the other hand, chiral amino alcohol-based ligands are of current interest because of their application in various asymmetric catalytic reactions (Banphavichit *et al.*, 2004; Lu *et al.*, 2001). We report here the synthesis and crystal structure (Fig. 1) of a new chiral Schiff base, (I), derived from 5-nitrosalicylaldehyde and L-phenylalaninol, in which intramolecular proton transfer occurs from the hydroxyl-O atom to the imine-N atom, through an $\text{O}-\text{H}\cdots\text{N}$ intramolecular hydrogen bond.



The title compound crystallizes with two molecules in the asymmetric unit, related by a non-crystallographic inversion centre at $(\frac{1}{4}, 0, \frac{1}{4})$. Some important bond lengths and angles are given in Table 1. The intramolecular hydrogen-bonding parameters are given in Table 2; these are comparable to those reported for similar systems (Dominiak *et al.*, 2003). The rather short distances observed for the bonds C2—C3 [1.351 (4) Å], C4—C5 [1.370 (3) Å], C18—C19 [1.359 (4) Å] and C20—C21 [1.358 (4) Å], in comparison with the regular aromatic distances, suggest a contribution from a quinoid structure, as expected for NH tautomers. The short distances O1—C1 = 1.266 (3) Å and O5—C17 = 1.267 (3) Å also support a quinoid structure. The presence of an NO_2 group in the *para* position is expected to play a role in stabilizing the present NH tautomeric form of the molecule.

Experimental

L-Phenylalaninol [(S)-(-)-2-Amino-3-phenyl-1-propanol] (1 mmol, 0.151 g) and 5-nitrosalicylaldehyde [2-hydroxy-5-nitrobenzaldehyde] (1 mmol, 0.167 g) were stirred together in methanol (15 ml) for 1 h at 298 K. The resulting solution was filtered. Slow evaporation of the filtrate gave a yellowish orange precipitate of the Schiff base (76% yield). Single crystals of (I) suitable for X-ray analysis were grown by slow evaporation of a toluene solution.

Crystal data

$C_{16}H_{16}N_2O_4$
 $M_r = 300.31$
 Monoclinic, $P2_1$
 $a = 5.8623$ (8) Å
 $b = 8.1322$ (10) Å
 $c = 30.674$ (4) Å
 $\beta = 91.450$ (2)°
 $V = 1461.9$ (3) Å³
 $Z = 4$

$D_x = 1.364$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5910 reflections
 $\theta = 2.6$ – 25.4 °
 $\mu = 0.10$ mm⁻¹
 $T = 295$ (2) K
 Block, orange
 $0.33 \times 0.28 \times 0.17$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{min} = 0.968$, $T_{max} = 0.983$
 15286 measured reflections

3102 independent reflections
 2530 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.030$
 $\theta_{max} = 26.1$ °
 $h = -7 \rightarrow 7$
 $k = -10 \rightarrow 10$
 $l = -37 \rightarrow 37$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.108$
 $S = 1.03$
 3102 reflections
 407 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2 + 0.0745P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.005$
 $\Delta\rho_{max} = 0.16$ e Å⁻³
 $\Delta\rho_{min} = -0.14$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O5—C17	1.267 (3)	N2—C7	1.287 (4)
C21—C20	1.358 (4)	N2—C8	1.478 (3)
C21—C22	1.398 (4)	C5—C4	1.370 (3)
C20—C19	1.394 (4)	C5—C6	1.395 (4)
N4—C23	1.286 (3)	C6—C7	1.422 (4)
N4—C24	1.460 (3)	C6—C1	1.444 (4)
C22—C23	1.420 (3)	O1—C1	1.266 (3)
C22—C17	1.436 (4)	C4—C3	1.403 (4)
C17—C18	1.432 (4)	C1—C2	1.422 (4)
C18—C19	1.359 (4)	C2—C3	1.351 (4)
C20—C21—C22	120.3 (3)	C7—N2—C8	125.7 (3)
C21—C20—C19	120.8 (3)	C4—C5—H5	119.8
C23—N4—C24	123.5 (3)	C5—C6—C7	119.4 (3)
C21—C22—C23	117.7 (2)	C5—C6—C1	119.8 (2)
C21—C22—C17	120.9 (2)	C7—C6—C1	120.8 (3)
C23—C22—C17	121.3 (2)	C5—C4—C3	121.1 (3)
O5—C17—C18	123.2 (3)	O1—C1—C2	122.2 (3)
O5—C17—C22	121.3 (2)	O1—C1—C6	121.1 (3)
C18—C17—C22	115.5 (3)	C2—C1—C6	116.7 (3)
C19—C18—C17	122.2 (3)	C3—C2—C1	122.5 (3)
C18—C19—C20	120.2 (3)		

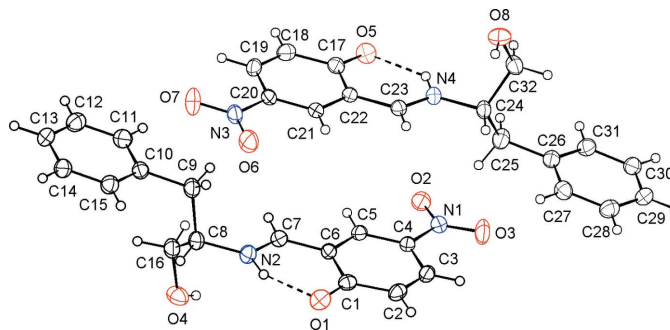


Figure 1

The structure of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level. The intramolecular hydrogen bonds are shown as dashed lines.

Table 2

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N2—H1A...O1	0.97 (3)	1.77 (3)	2.610 (3)	143 (3)
N4—H1B...O5	0.91 (3)	1.92 (3)	2.638 (3)	134 (3)

A non-crystallographic inversion centre close to $(\frac{1}{2}, 0, \frac{1}{2})$ relates the two independent molecules in the asymmetric unit, emulating space group $P2_1/n$ (e.g. Bats *et al.*, 2001). The actual space group is, however, $P2_1$, which is consistent with the fact that (I) is an enantiomerically pure compound. In the absence of significant anomalous scattering, Friedel pairs were merged, and the absolute configuration was assigned assuming that the configuration of the chiral starting material, L-phenylalaninol, was retained during the synthesis. The phenolic H atoms were located in a difference map, close to the imine-N atoms, and refined with free coordinates and isotropic U parameters. Other H atoms were placed in idealized positions and constrained to ride on their parent atoms; constrained distances: hydroxyl O—H = 0.82, aromatic C—H = 0.93 and methylene CH₂ = 0.97 Å. Isotropic displacement parameters were set to $U_{iso}(H) = 1.2U_{eq}(\text{carrier atom})$ for CH groups and $U_{iso}(H) = 1.2U_{eq}(\text{carrier atom})$ for hydroxyl groups.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2000); software used to prepare material for publication: SHELXTL.

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