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(−)-1-Benzyl-4-[1(*S*)-phenylethylamino]-5,6-dihydropyridin-2(1*H*)-one

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.004 Å
R factor = 0.034
wR factor = 0.090
Data-to-parameter ratio = 8.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title molecule, $C_{20}H_{22}N_2O$, the pyridine heterocycle has an envelope conformation. The crystal packing is stabilized by intermolecular N—H···O hydrogen bonds, which link the molecules into chains along the $[1\bar{1}0]$ direction.

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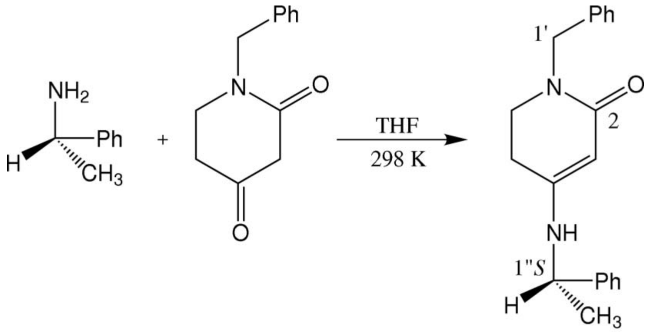
Comment

A general method for the preparation of enamines is to react aldehydes or ketones with secondary amines. The condensation reaction produces water, which should be removed using a Dean–Stark trap or molecular sieve. However, in some cases, there is no need to remove water, and the enamine is recovered in a quantitative yield. This is the case for the title compound, (I), which was prepared using a ketone and a chiral amine (see scheme and *Experimental*).



(I)

The conformation of the dihydro-1*H*-pyridine ring of (I) may be described as an envelope (Fig. 1), with atom C6 as the flap and a puckering amplitude (Cremer & Pople, 1975) of q = 0.419 (3) Å. This conformation results from the α,β-unsaturated system C4═C3—C2═O1, forcing this part of the molecule to be almost planar (r.m.s. deviation 0.074 Å). Related structures including a piperidone ring with a variety of substituents have been found to be stabilized with an envelope conformation (Beck *et al.*, 2004; Marin *et al.*, 2004; Romero *et al.*, 2005) or with a half-chair conformation distorted towards a screw boat (Waldmann *et al.*, 1990, 1991; Zukerman-Schpector *et al.*, 2001). This heterocycle thus seems to have a degree of conformational flexibility, which allows the accommodation of substituents with variable steric requirements.

Geometric parameters for (I) are in agreement with a π system delocalized from N1 to C7 (Table 1). However, compound (I) is an enamine rather than an imine, both in the solid state and in solution: the H atom bonded to N7 is easily found in a difference Fourier map and gives a doublet reso-

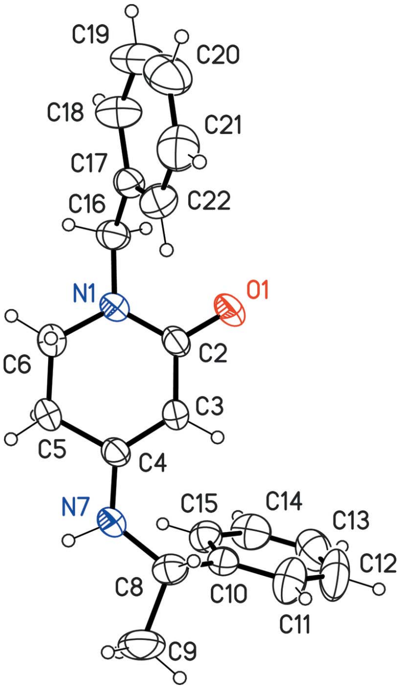


Figure 1
A view of (I), with displacement ellipsoids at the 40% probability level.

nance in the ^{1}H NMR spectrum, while the vinylic H atom gives a singlet signal, as expected for the enamine tautomer.

The crystal packing of (I) (Fig. 2) is stabilized by intermolecular N—H···O hydrogen bonds (Table 2), which link the molecules into chains along the [1$\overline{1}$0] direction.

Experimental

To a solution of (*S*)-(−)-phenylethylamine (0.65 mmol, 0.1 ml) in dry tetrahydrofuran (THF) (5 ml) was added a solution of 1-benzylpiperidine-2,4-dione (0.6 mmol, 120 mg) in dry THF (5 ml) and the mixture was stirred at 298 K for 12 h. The solvent was then removed and the crude product recrystallized from CH_2Cl_2/*n*-hexane (1:1) to give (I) (yield 100%). Spectroscopic analysis: $[\alpha]_D^{20} = -58.1$ (*c* 1.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, δ, p.p.m.): 1.40 (*d*, 3H, H9), 2.38 (*m*, 2H, H5), 3.18 (*dt*, 2H, H6), 4.40 (*t*, 1H, H8), 4.45 (*AB*, 2H, H16), 4.60 (*s*, 1H, H3), 5.20 (*d*, 1H, H7), 7.18–7.25 (*m*, 10H, Ph); ^{13}C NMR (100.6 MHz, $CDCl_3$, δ, p.p.m.): 23.64 (C9), 28.62 (C5), 43.78 (C6), 49.15 (C16), 52.80 (C8), 88.26 (C3), 125.50–128.40 (10 C, Ph), 138.00 (C-*ipso*), 143.20 (C-*ipso*), 154.10 (C4), 168.20 (C2).

Crystal data

$C_{20}H_{22}N_2O$
$M_r = 306.40$
Triclinic, *P*1
$a = 6.0091$ (7) Å
$b = 6.4829$ (8) Å
$c = 12.2030$ (15) Å
$\alpha = 81.136$ (10)°
$\beta = 80.670$ (10)°
$\gamma = 69.040$ (10)°
$V = 435.67$ (9) Å^3
$Z = 1$
$D_x = 1.168$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 77 reflections
$\theta = 3.6$–14.1°
$\mu = 0.07$ mm^{-1}
$T = 296$ (1) K
Prism, colourless
0.48 × 0.40 × 0.16 mm

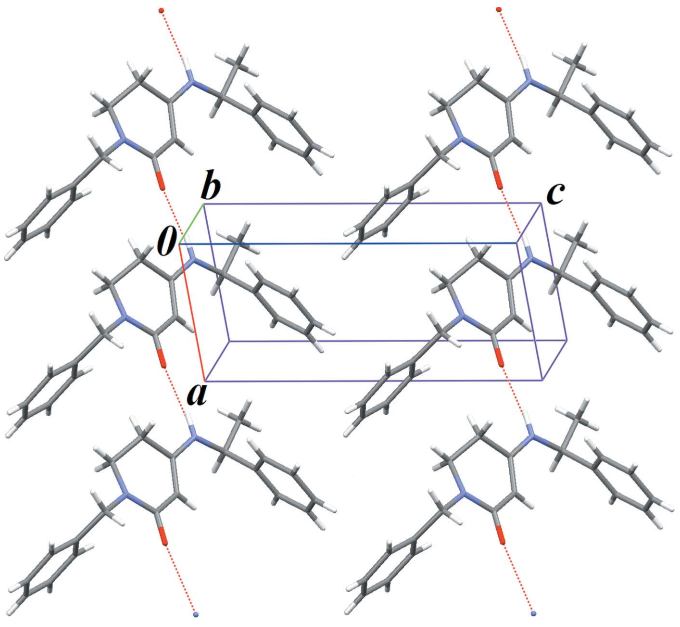


Figure 2
Part of the crystal structure of (I), showing the hydrogen-bonding scheme (dashed lines).

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: none
3488 measured reflections
1757 independent reflections
1481 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\rm max} = 26.3°$
$h = -7 \rightarrow 7$
$k = -8 \rightarrow 7$
$l = -15 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.090$
$S = 1.01$
1757 reflections
214 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2 + 0.0309P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.11$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.09$ e Å^{-3}
Extinction correction: *SHELXTL-Plus* (Sheldrick, 1998)
Extinction coefficient: 0.091 (12)

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.364 (3)	C3—C4	1.360 (3)
N1—C16	1.447 (3)	C4—N7	1.350 (3)
N1—C6	1.461 (3)	C4—C5	1.501 (3)
O1—C2	1.242 (3)	C5—C6	1.500 (3)
C2—C3	1.442 (3)	N7—C8	1.451 (3)
C2—N1—C16	119.82 (18)	C4—C3—C2	121.65 (19)
C2—N1—C6	119.26 (18)	N7—C4—C3	125.4 (2)
C16—N1—C6	119.90 (19)	N7—C4—C5	115.44 (18)
O1—C2—N1	119.5 (2)	C3—C4—C5	119.07 (18)
O1—C2—C3	122.2 (2)	C4—N7—C8	124.88 (19)
N1—C2—C3	118.27 (17)		

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N7—H7A⋯O1^{i}	0.90 (3)	1.96 (3)	2.850 (3)	171 (3)

Symmetry code: (i) $x-1, y+1, z$.

The H atom bonded to N7 was found in a difference Fourier map and refined with free coordinates and an isotropic U parameter. The C-bound H atoms were placed in idealized positions and refined as riding on their parent C atoms, with the following constraints: methine C—H = 0.98 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C); methylene C—H = 0.97 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C); methyl C—H 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C); aromatic and vinylic C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). In the absence of significant anomalous scattering effects, Friedel pairs were merged, and the absolute configuration was assigned on the basis of the known configuration of the amine used as starting material.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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