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(6*R*,7a*S*)-1,3,5,6,7,7a-Hexahydro-3-(2-hydroxyphenyl)-1,1-diphenylpyrrolo[1,2-*c*][1,3]oxazol-6-ol

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The molecule of the title compound, $C_{24}H_{23}NO_3$, consists of five rings, of which the pyrrole ring and oxazole ring are not planar. The compound was designed as a catalyst of the asymmetric Baylis–Hillman reaction, but it only has poor catalysis activity. According to the crystal structure analysis, this might be caused by steric hindrance due to the intramolecular O—H···N hydrogen bond. In the crystal structure, the molecules are connected by O—H···O and C—H···O hydrogen bonds, forming chains along [010]. The chains further interact through C—H···O hydrogen bonds, stacking along [100]. In the third direction [001], there is only weak interaction, which explains the crystal habit of a thin plate.

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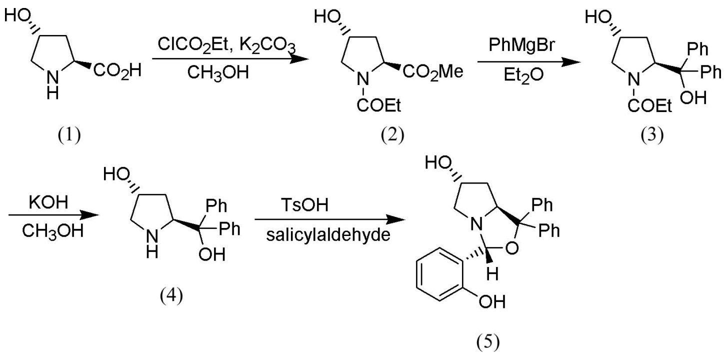
Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.004 Å
R factor = 0.041
wR factor = 0.092
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.

Comment

Recently, the asymmetric Baylis–Hillman reaction, affording *β*-hydroxyenones (acrylates), has made great progress. Baylis and Hillman first reported the reaction of acetaldehyde with ethyl acrylate and acrylonitrile in the presence of a catalytic amount of strong Lewis bases, such as 1,4-diazabicyclo[2.2.2]octane (DABCO) (Baylis & Hillmam, 1972). However, the applications and usefulness of this reaction in several cases are hampered by low yields, high concentration of catalyst, long reaction times and limited scope of substrates. To overcome these problems, designing new chiral catalysts has been an important aim. According to Drewers *et al.* (1988) and Marko *et al.* (1997), an OH group suitably disposed on an amine catalyst exerts a marked effect on rate acceleration as well as asymmetric induction. They suggested that the OH group stabilizes the oxy anion intermediate through hydrogen bonding, which accelerates the aldol addition reaction and also creates an asymmetric environment in some cases. Following this proposal, the title compound, (5), was synthesized; this is a tertiary amine possessing an alcohol OH group attached to a chiral centre, and a phenol OH group.



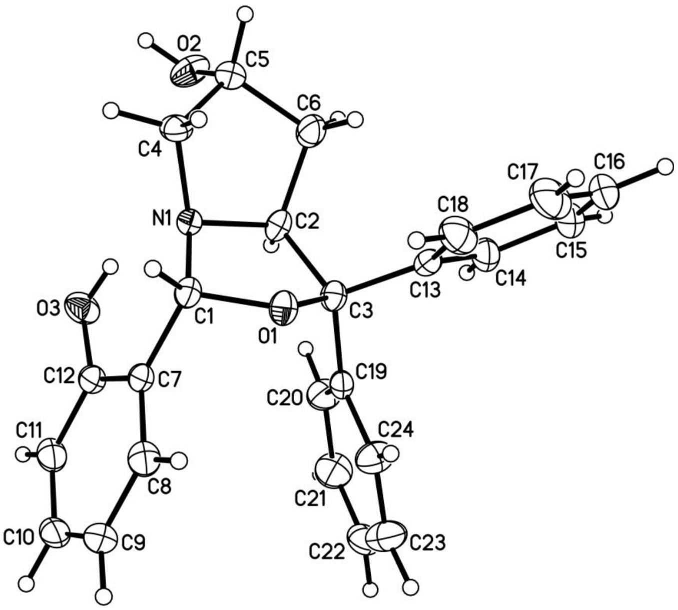


Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

The molecule contains five rings, of which the pyrrole ring and the oxazole ring are non-planar. The two five-membered rings display envelope conformations. Atom N1 deviates by 0.497 (2) Å from the plane formed by its three bonded atoms, namely C1, C2 and C4. There is a strong intramolecular O3—H3···N1 hydrogen bond (Table 2), which means that atom N1 is essentially inaccessible for intermolecular interaction. The ratio of its accessible free surface area to full surface area is only 7.15%, calculated by *OPEC* (Gavezzotti, 1983). Because atom N1 is almost completely surrounded by other atoms, it forms no intermolecular hydrogen bonds. This may be the main reason why (5) is a poor catalyst in the reaction. In the title crystal structure, molecules are connected by O—H···O and C—H···O hydrogen bonds along [010] (Table 2). The chains further interact through C—H···O hydrogen bonds (Desiraju, 1996, 2002), stacking along [100]. In the third direction [001], there is only weak van der Waals interactions, which explains the thin plate habit.

Experimental

The title compound was prepared as shown in the scheme in the *Comment*. Compound (4) was prepared from L-proline (1) according to the literature method of Corey & Bakshi (1990). A mixture of (4) (0.54 g, 2 mmol), salicylaldehyde (0.36 g, 3 mmol) and a catalytic amount of *p*-toluenesulfonic acid was refluxed for 6 h in a flask equipped with a Dean–Stark trap. The mixture was then neutralized with 5% $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with saturated NaCl solution before drying over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by recrystallization from Et_2O to give pure (5) [yield 0.50 g, 66.7%; m.p. 409–411 K; $[\alpha]D^2$ = −182.0 (*c* 1.0, $CHCl_3$)]. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.20–1.30 (*m*, 1H), 1.58–1.65, (*m*, 1H), 1.74–1.92 (*m*, 2H), 3.12 (*d, J* = 2.8 Hz, 2H), 4.50–4.54 (*m*, 1H), 4.93–4.98 (*m*, 1H), 5.48 (*s*, 1H), 6.71–7.60 (*m*, 14H), 11.60 (*bs*, 1H). Analysis calculated for $C_{24}H_{23}NO_3$ (%): C 77.19, H 6.21, N 3.75; found (%): C 76.91, H 6.33, N 3.89. MS *m/z* (%): 373.1661 (21.2%, M^+, calculated mass: 373.1678), 191.0946 (100%, M − Ph_2CO, calculated mass: 191.0946).

Crystal data

$C_{24}H_{23}NO_3$
$M_r = 373.43$
Orthorhombic, $P2_12_12_1$
$a = 6.0329$ (5) Å
$b = 9.4215$ (10) Å
$c = 33.796$ (4) Å
$V = 1920.9$ (3) Å^3
$Z = 4$
$D_x = 1.291$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 6890 reflections
$\theta = 3.0$–25.3°
$\mu = 0.09$ mm^{-1}
$T = 193$ (2) K
Plate, colorless
0.60 × 0.39 × 0.11 mm

Data collection

Rigaku Mercury diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{min} = 0.951$, $T_{max} = 0.991$
17845 measured reflections
2077 independent reflections

1962 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 25.4°$
$h = -7 \rightarrow 7$
$k = -11 \rightarrow 11$
$l = -36 \rightarrow 40$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.092$
$S = 1.15$
2077 reflections
254 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 0.4787P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.439 (3)	C1—C7	1.519 (3)
O1—C3	1.448 (3)	C2—C6	1.530 (4)
O2—C5	1.417 (3)	C2—C3	1.570 (3)
O3—C12	1.369 (3)	C3—C13	1.523 (3)
N1—C1	1.460 (3)	C3—C19	1.536 (3)
N1—C4	1.483 (3)	C4—C5	1.505 (3)
N1—C2	1.498 (3)	C5—C6	1.498 (3)
C1—O1—C3	107.49 (17)	O1—C3—C19	108.96 (19)
C1—N1—C4	114.10 (19)	C13—C3—C19	108.40 (18)
C1—N1—C2	106.83 (17)	O1—C3—C2	102.98 (16)
C4—N1—C2	106.85 (18)	C13—C3—C2	112.0 (2)
O1—C1—N1	105.92 (18)	C19—C3—C2	116.1 (2)
O1—C1—C7	112.82 (19)	N1—C4—C5	104.0 (2)
N1—C1—C7	112.7 (2)	O2—C5—C6	109.0 (2)
N1—C2—C6	104.80 (19)	O2—C5—C4	112.5 (2)
N1—C2—C3	104.82 (18)	C6—C5—C4	101.4 (2)
C6—C2—C3	117.3 (2)	C5—C6—C2	105.0 (2)
O1—C3—C13	107.97 (18)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···N1	0.84	1.83	2.583 (3)	148
O2—H2···O3^i	0.84	2.11	2.937 (3)	168
C11—H11···O2^{ii}	0.95	2.75	3.229 (3)	112
C4—H4*A*···O2^{iii}	0.99	2.80	3.687 (3)	149

Symmetry codes: (i) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1+x, y, z$.

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In the absence of significant anomalous scattering, Friedel pairs were merged before the final refinement. The absolute configuration was known from the synthesis. H atoms were positioned geometrically (O—H = 0.84, C—H = 0.95–1.00 Å) and refined as riding, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) or 1.5$U_{\rm eq}$(O).

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CrystalClear*; software used to prepare material for publication: *SHELXL97*.

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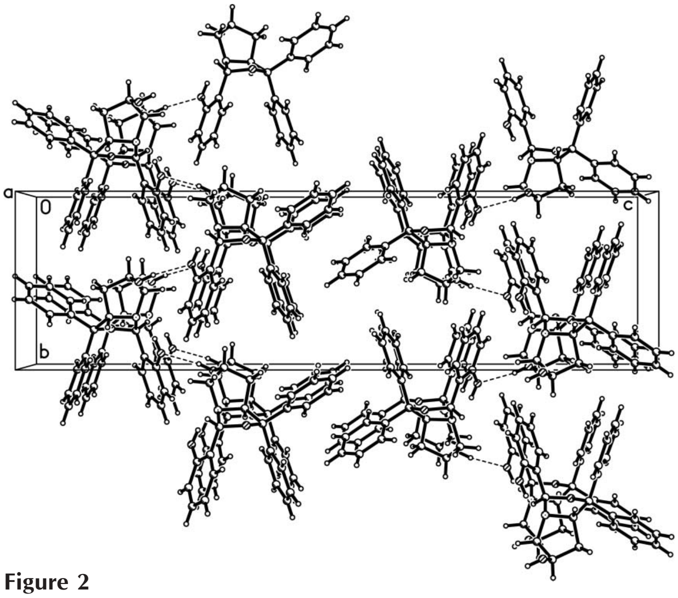

Figure 2
Packing diagram of (5), viewed down the *a* axis. Dashed lines indicate hydrogen bonds.

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