Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

2-[Hydroxy(2-pyridyl)methyl]-2-cyclopenten-1-one: the Baylis–Hillman adduct of 2-pyridinecarboxaldehyde and 2-cyclopenten-1-one

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Received 12 December 2003
Accepted 5 January 2004
Online 17 January 2004

In the title compound, $C_{11}H_{11}NO_2$, the cyclopentene ring is planar to within ±0.025 (2) Å. The dihedral angle between the cyclopentene plane and the pyridine ring plane is 83.1 (1)°. Strong intermolecular O—H···N hydrogen bonds link the molecules into a chain which runs parallel to the *a* axis and has a graph-set motif of *C*(5). Weak C—H···O interactions form a three-dimensional network in the crystal stucture.

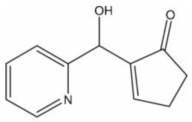
Key indicators

Single-crystal X-ray study
T = 293 K
Mean *σ*(C–C) = 0.003 Å
R factor = 0.035
wR factor = 0.095
Data-to-parameter ratio = 9.6

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

Comment

The Baylis–Hillman reaction (Baylis & Hillman, 1972), the coupling of activated alkenes with carbon electrophiles under the catalysis of tertiary amines, is emerging as a valuable C—C bond-forming reaction. Though other Baylis–Hillman products, synthesized from 2-pyridinecarboxaldehyde and vinyl compounds involving acrylamide, acrylate esters and acrylonitrile, have been reported (Ameer *et al.*, 1988; Bode & Kate, 1990, 1993), the adduct of 2-pyridinecarboxaldehyde and 2-cyclopenten-1-one, namely 2-[hydroxy(2-pyridyl)-methyl]-2-cyclopenten-1-one, (I), has not been reported previously. Like methyl 3-hydroxy-2-methyene-3-(2-pyridyl)-propionate (Bode & Kate, 1990, 1993), the title compound will be a useful intermediate in organic synthesis, even leading to applications in biology (Kabat *et al.*, 1996; Kim *et al.*, 2002; Shi & Zhao, 2002; Smith *et al.*, 1980). Here, we report the synthesis and crystal and molecular structures of (I).



(I)

The molecular configuration of (I) is shown in Fig. 1 and geometric parameters are listed in Table 1. The cyclopentene ring is planar to within 0.025 (2) Å. Atom C6 is coplanar with the pyridine ring plane but it deviates from the cyclopentene plane by 0.112 (2) Å. The dihedral angle between the cyclopentene plane and the pyridine ring plane is 83.1 (1)°.

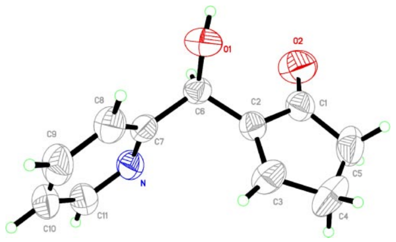


Figure 1
A view of the molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

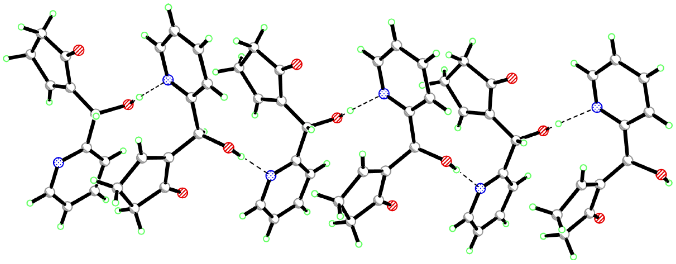


Figure 2
A view of the helical chain along the *a* axis. Hydrogen bonds are indicated by dashed lines.

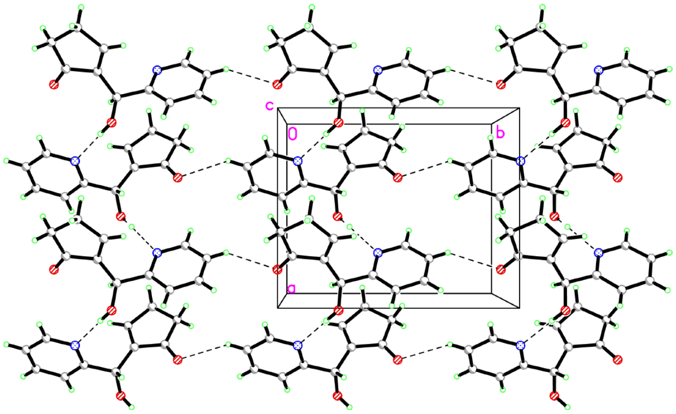


Figure 3
A packing diagram of (I), viewed down the *c* axis. Hydrogen bonds are indicated by dashed lines.

The screw-related molecules of (I) are linked by O—H···N hydrogen bonds (Table 2), with the hydroxyl O atom as a donor and the pyridine N atom acting as an acceptor, forming a helical chain along the *a* axis (Fig. 2). This chain has a graph-set motif *C*(5) (Bernstein *et al.*, 1995). Intermolecular C—H···O interactions (Desiraju, 1996; Steiner, 1997), with C···O distances in the range 3.154 (3)–3.319 (3) Å (Table 2), play a role in forming a three-dimensional network in the crystal stucture of (I). One of these weak interactions, C2—H10···O2(x, $y-1$, z), links the molecules into a chain which runs parallel to the *b* axis and has graph-set motif *C*(9) (Fig. 3). An intramolecular C—H···O interaction is also observed in the molecular structure.

Experimental

The title compound, 2-[hydroxy(2-pyridyl)methyl]-2-cyclopenten-1-one, (I), was synthesized *via* Baylis–Hillman reactions, according to the method reported by Luo *et al.* (2002). At room temperature, a clear solution of 2-pyridinecarboxaldehyde (1 mmol), cyclopent-2-enone (2 mmol) and imidazole (1 mmol) in tetrahydrofuran (1 ml) was charged with deionized water (1 ml). The mixture was stirred at ambient temperature for 20 h to complete the reaction. The mixture was diluted with water (10 ml) and extracted with ethyl acetate. The organic layer was concentrated under reduced pressure. After the usual work up, chromatography of the crude product on silica gel, using ethyl acetate and petroleum (1:1) as eluent, gave pure (I) as the product, with a yield of 94% (m.p. 388 K). Spectroscopic analysis: ^{1}H NMR (300 MHz, $CDCl_3$, δ, p.p.m.): 7.29–8.56 (*m*, 5H), 6.01 (*m*, 1H, *CH), 5.40 (*br*, 1H, OH), 2.49–2.63 (*m*, 4H, CH_2). The compound (100 mg) was dissolved in a mixed solvent of $CHCl_3$ (2 ml) and CH_2Cl_2 (2 ml). The solution was allowed to evaporate slowly at room temperature for several days, to obtain colourless crystals of (I).

Crystal data

$C_{11}H_{11}NO_2$
$M_r = 189.21$
Orthorhombic, $P2_12_12_1$
$a = 8.427$ (2) Å
$b = 10.200$ (2) Å
$c = 11.163$ (3) Å
$V = 959.5$ (4) Å^3
$Z = 4$
$D_x = 1.310$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 4137 reflections
$\theta = 2.7$–22.9°
$\mu = 0.09$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.30 × 0.20 × 0.20 mm

Data collection

Bruker SMART 1 K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.973$, $T_{\max} = 0.982$
5333 measured reflections
1217 independent reflections
1108 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\max} = 27.0°$
$h = -9 \rightarrow 10$
$k = -13 \rightarrow 11$
$l = -14 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.095$
$S = 1.06$
1217 reflections
127 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 0.1216P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.14$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N—C7	1.338 (2)	C2—C6	1.501 (3)
C7—C8	1.379 (3)	C2—C1	1.473 (3)
C8—C9	1.389 (3)	C2—C3	1.327 (3)
C9—C10	1.359 (3)	C4—C3	1.487 (3)
C10—C11	1.365 (3)	C5—C4	1.522 (4)
N—C11	1.339 (3)	C1—C5	1.502 (3)
C7—C6	1.512 (2)	O2—C1	1.211 (3)
O1—C6	1.418 (2)		
C7—N—C11	117.83 (17)	C2—C6—C7	111.94 (15)
N—C7—C8	121.99 (17)	C3—C2—C1	108.57 (19)
C7—C8—C9	118.6 (2)	C3—C2—C6	130.34 (18)
C10—C9—C8	119.5 (2)	C1—C2—C6	121.05 (17)
C9—C10—C11	118.5 (2)	O2—C1—C2	125.5 (2)
N—C11—C10	123.5 (2)	O2—C1—C5	126.5 (2)
N—C7—C6	115.52 (15)	C2—C3—C4	114.2 (2)
C8—C7—C6	122.48 (17)	C2—C1—C5	107.9 (2)
O1—C6—C2	109.67 (15)	C3—C4—C5	103.66 (18)
O1—C6—C7	109.65 (15)	C1—C5—C4	105.45 (19)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N$^{\rm i}$	0.82	1.98	2.796 (2)	178
C11—H11···O2$^{\rm ii}$	0.93	2.58	3.154 (3)	120
C9—H9···O1$^{\rm iii}$	0.93	2.60	3.293 (3)	132
C10—H10···O2$^{\rm iv}$	0.93	2.56	3.319 (3)	139
C8—H8···O1	0.93	2.42	2.746 (3)	100

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

H atoms were placed in calculated positions and allowed to ride on their parent atoms, with $U_{\rm iso}$(H) values set to $1.5U_{\rm eq}$(parent atom) for the hydroxyl H atom and $1.2U_{eq}$(parent atom) for the remaining H atoms. The O—H distance was fixed at 0.82 Å and the C—H distances were fixed in the range 0.93–0.98 Å. A rotating-group model was used for the hydroxyl group. Friedel pairs were merged before the final refinement

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

The authors are grateful for support from the National Natural Science Foundation of China and the Provincial Natural Science Foundation of Shanxi.

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