

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)
$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^*$$

	x	y	z	U_{eq}
P(1)	0.69791 (5)	0.18583 (5)	0.20206 (7)	0.0407
O(1)	0.7500	0.2483 (2)	0.0000	0.0649
C(1)	0.7293 (2)	0.1297 (2)	0.0945 (3)	0.0482
C(2)	0.7500	0.1760 (3)	0.0000	0.0490
C(3)	0.7591 (2)	0.2551 (2)	0.2632 (3)	0.0434
C(4)	0.8247 (2)	0.2398 (2)	0.2609 (3)	0.0531
C(5)	0.8715 (2)	0.2904 (3)	0.3158 (4)	0.0691
C(6)	0.8535 (3)	0.3546 (3)	0.3728 (4)	0.0690
C(7)	0.7890 (3)	0.3693 (2)	0.3744 (3)	0.0657
C(8)	0.7408 (2)	0.3206 (2)	0.3204 (3)	0.0560
C(9)	0.6818 (2)	0.1187 (2)	0.3112 (3)	0.0426
C(10)	0.6705 (2)	0.1465 (2)	0.4155 (3)	0.0536
C(11)	0.6595 (2)	0.0964 (2)	0.5000 (3)	0.0571
C(12)	0.6594 (3)	0.0183 (3)	0.4828 (4)	0.0675
C(13)	0.6701 (4)	-0.0100 (3)	0.3810 (4)	0.0971
C(14)	0.6816 (3)	0.0389 (2)	0.2942 (4)	0.0792
C(15)	0.6222 (2)	0.2324 (2)	0.1429 (3)	0.0492
C(16)	0.5640 (2)	0.1943 (3)	0.1458 (4)	0.0710
C(17)	0.5057 (3)	0.2268 (4)	0.0946 (5)	0.0961
C(18)	0.5064 (3)	0.2961 (3)	0.0400 (5)	0.0953
C(19)	0.5629 (3)	0.3348 (3)	0.0361 (5)	0.0920
C(20)	0.6219 (3)	0.3031 (3)	0.0869 (5)	0.0769
S(1)	0.60965 (6)	0.49694 (6)	0.33941 (9)	0.0609
O(2)	0.6513 (2)	0.5262 (3)	0.2651 (3)	0.1137
O(3)	0.6266 (2)	0.5202 (2)	0.4532 (3)	0.1269
O(4)	0.5948 (2)	0.4158 (2)	0.3302 (4)	0.1162
C(21)	0.5332 (4)	0.5408 (5)	0.2930 (8)	0.1251
F(1)	0.4864 (2)	0.5200 (3)	0.3461 (6)	0.1890
F(2)	0.5368 (3)	0.6161 (3)	0.2966 (7)	0.2551
F(3)	0.5134 (3)	0.5211 (4)	0.1830 (5)	0.2397

C(11)—C(10)—C(9)	120.6 (4)	F(3)—C(21)—F(1)	105.4 (7)
C(12)—C(11)—C(10)	120.6 (4)	F(3)—C(21)—F(2)	106.8 (7)
C(13)—C(12)—C(11)	119.5 (4)		

Symmetry code: (i) $\frac{1}{2} - x, y, -z$.

Reaction of trifluoromethane sulfonic acid anhydride with 1,3-bis(triphenylphosphoranylidene)acetone in benzene, followed by fractional crystallization in dichloromethane and diethyl ether, yielded the title compound as well as 1,3-propadienediylbis(triphenylphosphonium) bis(trifluoromethanesulfonate) (Bram, Burzlaff, Hadawi & Bestmann, 1992).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71102 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1045]

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Table 2. Geometric parameters (\AA , $^\circ$)

P(1)—C(1)	1.787 (4)	C(12)—C(13)	1.345 (7)
P(1)—C(3)	1.796 (3)	C(13)—C(14)	1.371 (6)
P(1)—C(9)	1.794 (3)	C(15)—C(16)	1.365 (6)
P(1)—C(15)	1.792 (4)	C(15)—C(20)	1.377 (5)
O(1)—C(2)	1.233 (6)	C(16)—C(17)	1.374 (7)
C(1)—C(2)	1.483 (5)	C(17)—C(18)	1.348 (7)
C(3)—C(4)	1.376 (6)	C(18)—C(19)	1.343 (8)
C(3)—C(8)	1.389 (5)	C(19)—C(20)	1.377 (6)
C(4)—C(5)	1.380 (6)	S(1)—O(2)	1.407 (4)
C(5)—C(6)	1.367 (7)	S(1)—O(3)	1.395 (3)
C(6)—C(7)	1.351 (7)	S(1)—O(4)	1.419 (3)
C(7)—C(8)	1.374 (6)	S(1)—C(21)	1.752 (8)
C(9)—C(10)	1.373 (5)	C(21)—F(1)	1.274 (9)
C(9)—C(14)	1.376 (5)	C(21)—F(2)	1.288 (9)
C(10)—C(11)	1.360 (5)	C(21)—F(3)	1.345 (9)
C(11)—C(12)	1.348 (6)		
C(3)—P(1)—C(1)	109.5 (2)	C(14)—C(13)—C(12)	121.4 (4)
C(9)—P(1)—C(1)	107.1 (2)	C(13)—C(14)—C(9)	119.4 (4)
C(9)—P(1)—C(3)	109.0 (1)	C(16)—C(15)—P(1)	119.4 (3)
C(15)—P(1)—C(1)	110.1 (2)	C(20)—C(15)—P(1)	121.2 (3)
C(15)—P(1)—C(3)	112.2 (2)	C(20)—C(15)—C(16)	119.3 (4)
C(15)—P(1)—C(9)	108.7 (2)	C(17)—C(16)—C(15)	120.3 (4)
C(2)—C(1)—P(1)	115.1 (3)	C(18)—C(17)—C(16)	119.6 (5)
C(1)—C(2)—O(1)	122.3 (2)	C(19)—C(18)—C(17)	121.3 (5)
C(1)—C(2)—C(1 ¹)	115.5 (4)	C(20)—C(19)—C(18)	119.9 (5)
C(4)—C(3)—P(1)	119.6 (3)	C(19)—C(20)—C(15)	119.6 (5)
C(8)—C(3)—P(1)	120.2 (3)	O(3)—S(1)—O(2)	114.5 (3)
C(8)—C(3)—C(4)	120.0 (3)	O(4)—S(1)—O(2)	116.3 (3)
C(5)—C(4)—C(3)	119.1 (4)	O(4)—S(1)—O(3)	111.8 (3)
C(6)—C(5)—C(4)	120.9 (5)	C(21)—S(1)—O(2)	104.7 (4)
C(7)—C(6)—C(5)	119.7 (4)	C(21)—S(1)—O(3)	105.2 (4)
C(8)—C(7)—C(6)	121.3 (4)	C(21)—S(1)—O(4)	102.7 (3)
C(7)—C(8)—C(3)	119.0 (4)	F(1)—C(21)—S(1)	115.7 (6)
C(10)—C(9)—P(1)	119.9 (3)	F(2)—C(21)—S(1)	111.8 (6)
C(14)—C(9)—P(1)	121.6 (3)	F(2)—C(21)—F(1)	107.8 (9)
C(14)—C(9)—C(10)	118.5 (4)	F(3)—C(21)—S(1)	108.8 (7)

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Structure of 2-(α -Hydroxybenzyl)-8-methyl-8-azabicyclo[3.2.1]octan-3-one

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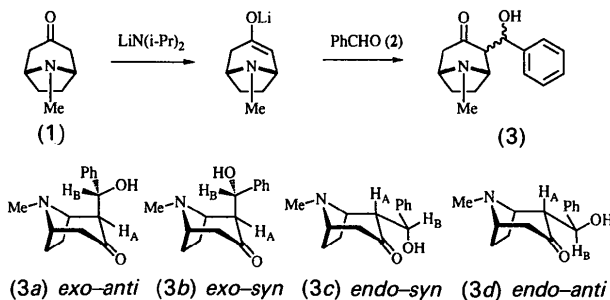
Abstract

The unambiguous structure of the title compound (which was formed in the reaction of the lithium enolate of tropinone with benzaldehyde) has been determined to be the *exo-anti* diastereoisomer. The piperidine ring adopts a flattened-chair conformation with the carbonyl group pushed away from the ethylene bridge. There is an intermolecular hydrogen bond between the hydroxyl group

and the N atom which replaces the intramolecular O—H···N hydrogen bond indicated by solution NMR data.

Comment

During a study investigating the enantioselective deprotonation of ketones of C_s symmetry, we deprotonated tropinone (1) with lithium diisopropylamide and reacted the resulting racemic enolate with benzaldehyde (2) producing selectively a racemic mixture of only one of four possible diastereoisomeric aldols (3a)–(3d) (Majewski & Zheng, 1991), as shown in the scheme below. Compounds of this type are important intermediates in the synthesis of tropane alkaloids (Lounasmaa, 1988).



The vicinal coupling constant, J_{AB} , in the NMR spectrum of product (3) was 3.0 Hz. It is well known (Heathcock, 1984) that aldols usually exist in solution in a hydrogen-bonded form (OH forms an intramolecular hydrogen bond to the carbonyl O atom) and, as a result, the *syn* (*erythro*) aldols usually have J_{AB} in the range 2–6 Hz, whereas for the *anti* (*threo*) aldols J_{AB} is normally 7–10 Hz (Heathcock, 1984). The small coupling constant seemed to suggest the *syn* stereochemistry for our product [(3b) or (3c)]. However, since it is also well known that cyclic enolates yield predominantly *anti* aldols (Majewski & Gleave, 1989), we hypothesized that the structure of our product should be *exo-anti* (3a). We reasoned that the unusually small vicinal coupling constant, J_{AB} , may result from the hydrogen bonding between the OH and the N atom in (3a) (in solution). Examination of models has shown that the conformer of (3a), in which such hydrogen bonding existed, would have a dihedral angle $\text{H}_2\text{—C}_2\text{—C}_1'\text{—H}_1'$ of 66° ; this would explain the small J_{AB} value (Silverstein, Bassler & Morrill, 1991). Nuclear Overhauser enhancement measurements on a derivative indicated agreement with structure (3a) (Majewski & Zheng, 1991). It should be noted that even though NMR spectroscopy has been used extensively in the analysis of the structures and conformations of tropane alkaloids, some results have been questioned (Lounasmaa, 1988; Bachmann & von Philipsborn, 1972). Unambiguous determination of the structure of (3) by X-ray crystallography therefore seemed necessary, especially if the NMR data for this compound are to be used for fu-

ture structure- and conformation-elucidation studies of tropane alkaloids.

A stereoscopic view of the title compound is illustrated in Fig. 1. The bond distances and angles lie within the normal range. The chair-type piperidine ring (C1—C2—C3—C4—C5—N) is significantly flattened at C3; the atoms C1, C2, C4, C5 are coplanar to within 0.0125 \AA , with C3 and N displaced on opposite sides of this plane by -0.506 and $+0.859 \text{ \AA}$, respectively. Similar conformations were observed in earlier studies (Jones & Hamor, 1985; Hamor & Kings, 1980; Vooren, Schenk & MacGillavry, 1970). The five-membered ring C1—N—C5—C6—C7 is in the envelope conformation; C1, C5, C6, C7 are coplanar to within 0.0046 \AA with the N atom displaced by $+0.65 \text{ \AA}$ from this plane.

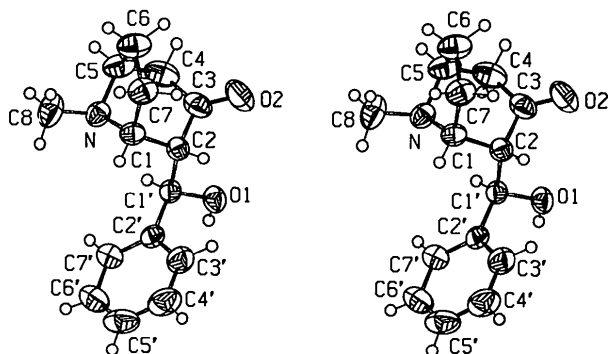


Fig. 1. Stereoscopic view of the title molecule.

The reaction of the lithium enolate of tropinone with benzaldehyde yields the *exo-anti* diastereoisomer of 2-(α-hydroxybenzyl)-8-methyl-8-azabicyclo[3.2.1]octan-3-one. There is no intramolecular hydrogen bonding in this structure, but there is an intermolecular hydrogen bond between O1 and Nⁱ [$\text{O}1\cdots\text{N}^i$ 2.842 (3) Å, $\text{O}1\text{—H}10\cdots\text{N}^i$ 168 (3)°; symmetry code: (i) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$]. The existence of an intermolecular hydrogen bond between O1 and Nⁱ indicates that an O—H···N bond is preferred over an O—H···O (carbonyl) bond in the title compound. The intermolecular hydrogen bond is apparently broken in solution by a rotation of the C2—C1' bond and is replaced by an intramolecular hydrogen bond between O1 and N, as suggested by the NMR evidence.

Experimental

Crystal data

$\text{C}_{15}\text{H}_{19}\text{NO}_2$
 $M_r = 245.3$
 Orthorhombic
Pbca
 $a = 8.1213 (7) \text{ \AA}$
 $b = 17.514 (3) \text{ \AA}$
 $c = 18.903 (3) \text{ \AA}$

Cu $K\alpha$ radiation
 $\lambda = 1.5418 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 19.03\text{--}39.72^\circ$
 $\mu = 6.470 \text{ mm}^{-1}$
 $T = 287 \text{ K}$

$V = 2688.7$ (7) Å³
 $Z = 8$
 $D_x = 1.212$ Mg m⁻³
 $D_m = 1.234$ Mg m⁻³
 Density measured by flotation

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 2845 measured reflections
 2752 independent reflections
 1895 observed reflections
 $[I > 2.0\sigma(I)]$

Refinement

Refinement on F^2
 Final $R = 0.048$
 $wR = 0.059$
 $S = 2.619$
 1895 reflections
 240 parameters
 All H-atom parameters refined
 $w = 1/\sigma^2(F_o)$
 $(\Delta/\sigma)_{\max} = 0.123$

Prism
 $0.42 \times 0.25 \times 0.15$ mm
 Colorless

$R_{\text{int}} = 0.002$
 $\theta_{\text{max}} = 74.8^\circ$
 $h = 0 \rightarrow 10$
 $k = 0 \rightarrow 21$
 $l = 0 \rightarrow 23$
 3 standard reflections
 frequency: 333 min
 intensity variation: none

$\Delta\rho_{\text{max}} = 0.374$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.317$ e Å⁻³
 Extinction correction: Gaussian (Zachariasen)
 Extinction coefficient: $9(2) \times 10^{-6}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: Enraf-Nonius (1981) CAD-4 PDP8 software. Cell refinement: Enraf-Nonius (1981) CAD-4 PDP8 software. Data reduction: *Xtal DIFDAT, ADDREF, SORTRF* (Hall & Stewart, 1990). Program(s) used to solve structure: *Xtal GENEV, GENSIN, GENTAN*. Program(s) used to refine structure: *Xtal CRYLSQ*. Molecular graphics: *Xtal ORTEP, PLOTX*. Software used to prepare material for publication: *Xtal BONDLA, LISTFC, CIFIO*.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)*

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
C1	0.8803 (3)	0.5884 (1)	0.4402 (1)	0.044 (1)
C2	0.7101 (3)	0.6268 (1)	0.4392 (1)	0.044 (1)
C3	0.6870 (4)	0.6672 (1)	0.3691 (1)	0.058 (2)
C4	0.8361 (4)	0.7092 (2)	0.3419 (2)	0.069 (2)
C5	0.9898 (4)	0.6612 (2)	0.3519 (1)	0.063 (2)
C6	0.9696 (5)	0.5819 (2)	0.3176 (2)	0.070 (2)
C7	0.8970 (4)	0.5325 (2)	0.3770 (1)	0.059 (2)
C8	1.1737 (4)	0.6160 (2)	0.4465 (2)	0.073 (2)
C1'	0.6852 (3)	0.6829 (1)	0.5011 (1)	0.041 (1)
C2'	0.6989 (3)	0.6452 (1)	0.5728 (1)	0.042 (1)
C3'	0.5879 (3)	0.5885 (2)	0.5931 (1)	0.061 (2)
C4'	0.5989 (4)	0.5557 (2)	0.6594 (2)	0.078 (2)
C5'	0.7177 (5)	0.5800 (2)	0.7063 (2)	0.076 (2)
C6'	0.8273 (4)	0.6355 (2)	0.6872 (1)	0.068 (2)
C7'	0.8181 (3)	0.6680 (1)	0.6199 (1)	0.052 (1)
N	1.0089 (2)	0.6465 (1)	0.4287 (1)	0.049 (1)
O1	0.5270 (2)	0.7162 (1)	0.49155 (9)	0.0516 (9)
O2	0.5594 (3)	0.6629 (1)	0.3363 (1)	0.090 (2)

Table 2. *Geometric parameters (Å, °)*

C1—C2	1.537 (3)	C8—N	1.480 (4)
C1—C7	1.551 (4)	C1'—C2'	1.512 (3)
C1—N	1.474 (3)	C1'—O1	1.423 (3)
C2—C3	1.514 (3)	C2'—C3'	1.394 (4)
C2—C1'	1.541 (3)	C2'—C7'	1.375 (3)
C3—C4	1.507 (4)	C3'—C4'	1.381 (4)
C3—O2	1.210 (4)	C4'—C5'	1.378 (5)
C4—C5	1.517 (5)	C5'—C6'	1.367 (5)
C5—C6	1.542 (4)	C6'—C7'	1.396 (4)
C5—N	1.481 (3)	O1—H10	0.93 (4)
C6—C7	1.534 (4)		
C2—C1—C7	110.2 (2)	C2—C1'—C2'	113.1 (2)
C2—C1—N	109.4 (2)	C2—C1'—O1	106.5 (2)
C7—C1—N	105.1 (2)	C2'—C1'—O1	111.1 (2)
C1—C2—C3	109.1 (2)	C1'—C2'—C3'	120.6 (2)
C1—C2—C1'	112.8 (2)	C1'—C2'—C7'	120.3 (2)
C3—C2—C1'	110.5 (2)	C3'—C2'—C7'	119.0 (2)
C2—C3—C4	115.3 (2)	C2'—C3'—C4'	120.2 (3)
C2—C3—O2	121.7 (2)	C3'—C4'—C5'	120.1 (3)
C4—C3—O2	123.0 (2)	C4'—C5'—C6'	120.4 (3)
C3—C4—C5	110.4 (2)	C5'—C6'—C7'	119.8 (3)
C4—C5—C6	111.0 (3)	C2'—C7'—C6'	120.6 (3)
C4—C5—N	107.8 (2)	C1—N—C5	101.0 (2)
C6—C5—N	105.4 (2)	C1—N—C8	111.0 (2)
C5—C6—C7	104.0 (2)	C5—N—C8	112.4 (2)
C1—C7—C6	103.9 (2)		

The θ -scan width was $(0.85 + 0.14 \tan \theta)^\circ$ with a θ -scan rate of $0.37\text{--}3.38^\circ \text{ min}^{-1}$. The scan angle was extended 25% on each side of each peak for background measurement. Refinement was by full-matrix least-squares methods.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55991 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1010]

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