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(3a*S*,3b*R*,6*R*,7a*R*)-2-Benzyl-1,2,3a,3b,4,7a-hexahydro-6-phenyl-3,5-dioxa-2,6a-diazacyclopenta[*a*]pentalen-7-one

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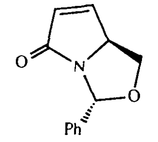
Abstract

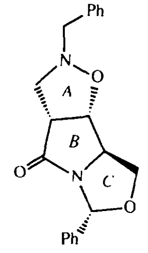
The cycloaddition of *N*-benzylnitrone and the known α,β-unsaturated bicyclic lactam derived from (*S*)-pyroglutaminol and benzaldehyde leads to the tricyclic title compound, $C_{20}H_{20}N_2O_3$. The central ring is nearly planar while the adjacent *cis*-fused rings have envelope conformations.

Comment

Conveniently *N*-protected α,β-unsaturated pyrrolidones can act as good dipolarophiles in the 1,3-dipolar cycloaddition of nitrones. Thus, an adduct was obtained (in 64% isolated yield) through the cycloaddition of *N*-benzylnitrone and the known α,β-unsaturated bicyclic lactam derived from (*S*)-pyroglutaminol and benzaldehyde, (1) (Hanessian & Ratovelomanana, 1990; Hamada, Hara, Kawai, Kohno & Shioiri, 1991; Griffart-Brunet & Langlois, 1994). The regioselectivity generally observed in such cycloadditions (Tufariello, 1984; Carruthers, 1990) and steric considerations support the structure (2). This structure could not be proven easily by ^1H NMR owing to the absence of coupling between the adjacent protons H—C3a and H—C3b and the broadening of signals due to relatively slow inversion of the isoxazolidine N atom. Thus, the structure of compound (2) was resolved unambiguously by an X-ray diffraction analysis.



(1)



(2)

The general shape of the molecule is shown in Fig. 1. The ring junction between rings *A* and *B* is *cis*. The oxazolidine ring *A* adopts an envelope conformation with the atom N2 at 0.568 (3) Å from the mean plane of the four other atoms. Ring *B* is nearly planar exhibiting a half-chair conformation. The atom N6a is out of the lactam ring plane [the sum of the three bond angles is 343.5° and the distance of N6a to the plane of the three bonded atoms is 0.336 (2) Å]. The five-membered rings *B* and *C* appear *cis*-fused. Ring *C* exhibits an envelope conformation with atom C3b 0.477 (2) Å out of the mean plane of the four other atoms.

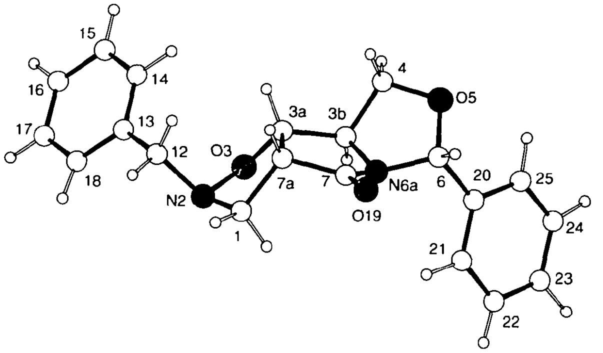


Fig. 1. The structure of compound (2) depicting the general shape of the molecule.

Experimental

Crystal data

$C_{20}H_{20}N_2O_3$
M_r = 336.39
Orthorhombic
$P2_12_12_1$
a = 5.607 (2) Å
b = 10.954 (3) Å
c = 27.452 (15) Å
V = 1686.1 (11) Å^3
Z = 4
D_x = 1.33 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 11.3–24.6°
μ = 0.69 mm^{-1}
T = 293 K
Prism
0.65 × 0.20 × 0.15 mm
Colourless

Data collection

Nonius CAD-4 diffractometer

$\theta/2\theta$ scans

Absorption correction: none

1807 measured reflections

1807 independent reflections

1678 observed reflections [$I > 3.0\sigma(I)$]

$\theta_{\max} = 67.76°$

$h = 0 \rightarrow 6$

$k = 0 \rightarrow 13$

$l = 0 \rightarrow 32$

3 standard reflections frequency: 166 min intensity variation: none

Refinement

Refinement on F

$R = 0.037$

$wR = 0.052$

$S = 1.04$

1676 reflections

306 parameters

All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.0023F^2]$

$(\Delta/\sigma)_{\max} = 0.06$

$\Delta\rho_{\max} = 0.17$ e Å^{-3}

$\Delta\rho_{\min} = -0.17$ e Å^{-3}

Extinction correction: none

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2*B*)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
C1	−0.0821 (5)	0.7085 (2)	0.1921 (1)	0.054 (2)
N2	−0.1867 (4)	0.8283 (2)	0.1820 (1)	0.046 (2)
O3	−0.1092 (3)	0.8494 (1)	0.1324 (1)	0.045 (1)
C3a	0.1328 (4)	0.8051 (2)	0.1277 (1)	0.039 (2)
C3b	0.1581 (4)	0.7377 (2)	0.0793 (1)	0.042 (2)
C4	0.3916 (6)	0.7551 (3)	0.0517 (1)	0.060 (2)
O5	0.4444 (4)	0.6401 (2)	0.0309 (1)	0.077 (2)
C6	0.3096 (4)	0.5456 (2)	0.0546 (1)	0.050 (2)
N6a	0.1772 (3)	0.6085 (2)	0.0925 (1)	0.043 (1)
C7	0.2241 (4)	0.5920 (2)	0.1411 (1)	0.048 (2)
C7a	0.1642 (4)	0.7094 (2)	0.1674 (1)	0.044 (2)
C12	−0.0813 (5)	0.9227 (2)	0.2136 (1)	0.047 (2)
C13	−0.1510 (4)	1.0499 (2)	0.1990 (1)	0.041 (2)
C14	0.0023 (4)	1.1216 (2)	0.1719 (1)	0.050 (2)
C15	−0.0533 (6)	1.2413 (2)	0.1601 (1)	0.059 (2)
C16	−0.2676 (6)	1.2906 (2)	0.1751 (1)	0.064 (3)
C17	−0.4231 (5)	1.2202 (3)	0.2019 (1)	0.067 (3)
C18	−0.3679 (4)	1.1000 (3)	0.2142 (1)	0.055 (2)
O19	0.2974 (5)	0.4984 (2)	0.1592 (1)	0.075 (2)
C20	0.1508 (4)	0.4826 (2)	0.0179 (1)	0.039 (1)
C21	−0.0563 (4)	0.4249 (2)	0.0330 (1)	0.046 (2)
C22	−0.2026 (5)	0.3657 (2)	−0.0004 (1)	0.058 (2)
C23	−0.1398 (6)	0.3644 (3)	−0.0491 (1)	0.065 (2)
C24	0.0664 (6)	0.4204 (3)	−0.0644 (1)	0.062 (2)
C25	0.2134 (5)	0.4785 (2)	−0.0312 (1)	0.052 (2)

Table 2. *Selected geometric parameters* (Å, °)

C1—N2	1.464 (3)	C7—O19	1.211 (3)
C1—C7a	1.538 (4)	C12—C13	1.501 (3)
N2—O3	1.446 (2)	C13—C14	1.383 (3)
N2—C12	1.474 (3)	C13—C18	1.398 (3)
O3—C3a	1.447 (3)	C14—C15	1.386 (4)
C3a—C3b	1.527 (2)	C15—C16	1.381 (4)
C3a—C7a	1.523 (3)	C16—C17	1.377 (4)
C3b—C4	1.525 (4)	C17—C18	1.395 (4)
C3b—N6a	1.464 (3)	C20—C21	1.386 (3)
C4—O5	1.415 (4)	C20—C25	1.392 (3)
O5—C6	1.436 (3)	C21—C22	1.390 (3)
C6—N6a	1.453 (3)	C22—C23	1.382 (4)
C6—C20	1.511 (3)	C23—C24	1.375 (4)
N6a—C7	1.373 (3)	C24—C25	1.385 (4)
C7—C7a	1.512 (3)		
N2—C1—C7a	105.7 (2)	C7a—C7—O19	126.8 (2)
C1—N2—O3	101.6 (2)	C1—C7a—C3a	102.5 (2)
C1—N2—C12	110.9 (2)	C1—C7a—C7	113.8 (2)
O3—N2—C12	108.8 (2)	C3a—C7a—C7	105.6 (2)
N2—O3—C3a	108.2 (1)	N2—C12—C13	112.9 (2)
O3—C3a—C3b	109.1 (2)	C12—C13—C14	120.6 (2)
O3—C3a—C7a	105.9 (2)	C12—C13—C18	120.7 (2)
C3b—C3a—C7a	106.2 (2)	C14—C13—C18	118.6 (2)
C3a—C3b—C4	116.8 (2)	C13—C14—C15	121.6 (2)
C3a—C3b—N6a	105.0 (2)	C14—C15—C16	119.8 (3)
C4—C3b—N6a	100.4 (2)	C15—C16—C17	119.4 (3)
C3b—C4—O5	105.6 (2)	C16—C17—C18	121.2 (3)
C4—O5—C6	110.5 (2)	C13—C18—C17	119.4 (2)
O5—C6—N6a	104.5 (2)	C6—C20—C21	120.1 (2)
O5—C6—C20	109.7 (2)	C6—C20—C25	120.7 (2)
N6a—C6—C20	113.2 (2)	C21—C20—C25	119.1 (2)
C3b—N6a—C6	108.6 (2)	C20—C21—C22	120.6 (2)
C3b—N6a—C7	112.4 (2)	C21—C22—C23	119.5 (2)
C6—N6a—C7	122.5 (2)	C22—C23—C24	120.4 (3)
N6a—C7—C7a	108.1 (2)	C23—C24—C25	120.2 (3)
N6a—C7—O19	125.1 (2)	C20—C25—C24	120.2 (2)
C1—N2—O3—C3a	−39.1 (2)	N6a—C3b—C4—O5	29.4 (2)
N2—O3—C3a—C7a	24.0 (2)	C3b—C4—O5—C6	−17.5 (2)
O3—C3a—C7a—C1	0.5 (2)	C4—O5—C6—N6a	−2.2 (2)
C3a—C7a—C1—N2	−24.1 (2)	O5—C6—N6a—C3b	22.3 (2)
C7a—C1—N2—O3	38.4 (2)	C6—N6a—C3b—C4	−31.7 (2)
C7a—C3a—C3b—N6a	5.6 (2)	C1—N2—C12—C13	170.2 (3)
C3a—C3b—N6a—C7	−14.6 (2)	O3—N2—C12—C13	59.2 (2)
C3b—N6a—C7—C7a	17.5 (2)	N2—C12—C13—C14	−99.6 (2)
N6a—C7—C7a—C3a	−12.9 (2)	O5—C6—C20—C25	27.4 (2)
C7—C7a—C3a—C3b	4.0 (2)	N6a—C6—C20—C21	−38.3 (2)

The isotropic temperature factors of the H atoms were set equal to $1.10U_{eq}$ of the bonded atom.

Data collection: CAD-4 diffractometer software (Enraf–Nonius, 1987). Data reduction: *NONIUS* (Riche, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *R3M* (Riche, 1983); *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *ACTACIF* (Riche, 1992).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1120). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(5*S*,*S*S)-7-Methyl-8-*p*-toluenesulfinyl-1,6-dioxaspiro[4.5]dec-7-ene

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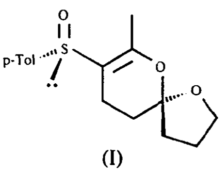
Abstract

The structure determination of $C_{16}H_{20}O_3S$ based on X-ray single-crystal diffraction confirms the *S* absolute configuration of the spiroketalic C atom.

Comment

The intermolecular hetero-Diels–Alder reaction between α,β-unsaturated carbonyl compounds and vinyl ethers has been applied extensively to the synthesis of natural products (Boger & Weinzed, 1987). In connection with our interest in using chiral sulfoxides in asymmetric syntheses, we sought new strategies for constructing spiroketal skeletons by heterocycloaddition using an enantiopure sulfinyl-hetero diene. (+)-(*S*)-3-*p*-Toluenesulfinyl-3-buten-2-one (Bonfand, Gosselin & Maignan, 1992) reacted smoothly with sensitive 2-methylene tetrahydrofuran yielding 1:1 diastereomeric dioxaspiro adducts. These spiroketals were completely separated by liquid chromatography on silica gel. In order to obtain information on the absolute configuration of the spirokelatic C atom, we obtained single crystals of one diastereomer, (I), with a view to determining its structure by X-ray diffraction.



(I)

The perspective view of the structure of (5*S*,*S*S)-7-methyl-8-*p*-toluenesulfinyl-1,6-dioxaspiro[4.5]dec-7-ene reveals the *S* absolute configuration of the spirokelatic atom, C11.

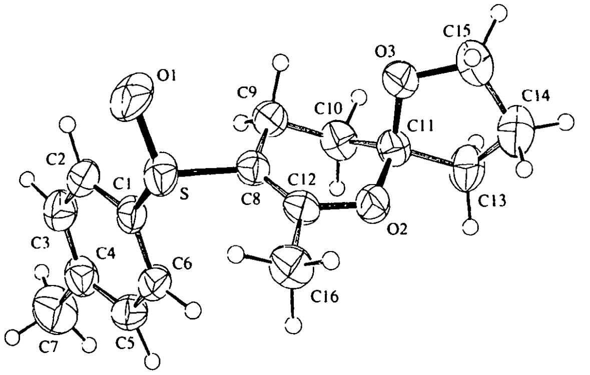


Fig. 1. *ORTEP* plot of $C_{16}H_{20}O_3S$. For the sake of clarity the displacement parameters of the H atoms have been divided by ten. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Recrystallization of the title compound from ether after liquid chromatography gave small colourless platelets. Suitable crystals for X-ray analysis were very difficult to find. Finally, a parallelepipedic crystal was chosen and its quality was tested using Laue photographs.

Crystal data

$C_{16}H_{20}O_3S$
$M_r = 292.37$
Orthorhombic
$P2_12_12_1$
$a = 7.9680\ (14)$ Å
$b = 8.1104\ (11)$ Å
$c = 23.761\ (3)$ Å
$V = 1535.5\ (4)$ Å^3
$Z = 4$
$D_x = 1.265$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 32 reflections
$\theta = 12.6–15.9°$
$\mu = 0.205$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.741 × 0.471 × 0.201 mm
Colourless

Data collection

Stoe Siemens AED-2 diffractometer
ω–2θ scans
Absorption correction: none
3115 measured reflections
2626 independent reflections
2268 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0602$
$\theta_{\rm max} = 25°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -28 \rightarrow 28$
3 standard reflections
frequency: 60 min
intensity variation: 8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0514$
$wR(F^2) = 0.1337$
$S = 1.046$
2619 reflections

Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.0069 (39)

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