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(5*S*)-3-Phenyl-5-[(6*R*,7*R*,14*R*)-1,8,13,16-tetraoxadispiro[5.0.5.4]hexadecan-14-yl]-4,5-dihydroisoxazole: the Major Adduct Resulting from Cycloaddition of Benzonitrile Oxide to (6*R*,7*R*,14*S*)-14-Vinyl-1,8,13,16-tetraoxadispiro[5.0.5.4]hexadecane

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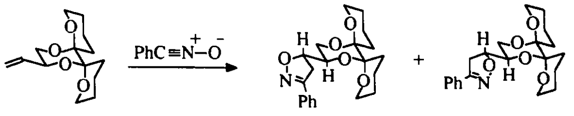
Abstract

This structure determination of $C_{21}H_{27}NO_5$, taken with the known absolute configuration of the starting alkene, establishes the configuration of the new stereogenic C5 centre in the title compound. The five-membered 4,5-dihydroisoxazole ring adopts a predominantly envelope conformation folded between the O1 and C4 atoms, and the two pyranoid rings and the 1,4-dioxane ring of the dispiroketal unit are in chair conformations.

Comment

As part of an investigation into the factors influencing stereoselectivity in nitrile oxide cycloadditions to chiral allyl ethers, the reaction of benzonitrile oxide ($PhC{\equiv}N^+{-}O^-$) with (6*R*,7*R*,14*S*)-14-vinyl-1,8,13,16-tetraoxadispiro[5.0.5.4]hexadecane, (1), has been examined (Gravestock, Paton & Todd, 1995). Two 4,5-dihydroisoxazole cycloadducts, (2) (52%) and (3) (16%), were isolated from the reaction mixture and the former provided crystals suitable for X-ray crystallography. Taken with the known absolute configuration of the starting alkene (1) (Ley, Woods & Zanotti-Gerosa, 1992), the present structure determination firmly establishes that the newly created stereogenic C5 centre in adduct (2) has an *S* configuration and that the minor isomer, (3), therefore has a 5*R* structure.



(1) (2) (3)

The Cremer & Pople (1975) puckering parameters for the four rings are given in Table 3. For the five-membered dihydroisoxazole ring, φ = 319.3 (5)°, which corresponds to a mainly envelope conformation *E*5 (φ = 324°), with the fold between the O1 and C4 atoms; the torsion angle for the O1—N2=C3—C4 unit is −2.6 (3)° and the C5 atom lies 0.406 (4) Å out of the best plane through these atoms. The θ values for the 1,4-dioxane ring and the two pyranoid rings indicate that the conformations of all three are very close to the ideal chair conformation (θ = 180°). No anomalies are found in the bond lengths and angles.

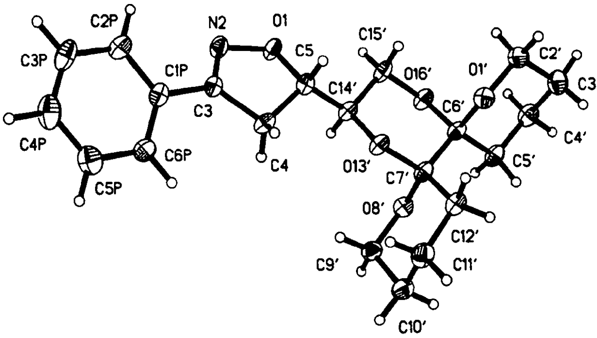


Fig. 1. A view of the title molecule, including the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compound was obtained by cycloaddition of benzonitrile oxide to (6*R*,7*R*,14*S*)-14-vinyl-1,8,13,16-tetraoxadispiro-[5.0.5.4]hexadecane as reported elsewhere (Gravestock, Paton & Todd, 1995).

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Crystal data

$C_{21}H_{27}NO_5$
$M_r = 373.44$
Monoclinic
$P2_1$
$a = 6.3561\,(14)$ Å
$b = 9.892\,(2)$ Å
$c = 14.937\,(3)$ Å
$\beta = 95.04\,(2)°$
$V = 935.6\,(3)$ Å^3
$Z = 2$
$D_x = 1.326$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 15–16°$
$\mu = 0.094$ mm^{-1}
$T = 293\,(2)$ K
Column
$0.78 \times 0.23 \times 0.16$ mm
Colourless

Data collection

Stoe diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1308 measured reflections
1308 independent reflections
1237 observed reflections
$[I > 2\sigma(I)]$

$\theta_{\max} = 22.53°$
$h = -6 \rightarrow 6$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: <1%

Refinement

Refinement on F^2
$R(F) = 0.0276$
$wR(F^2) = 0.0766$
$S = 1.095$
1304 reflections
272 parameters
H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.1692P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.043$
$\Delta\rho_{\max} = 0.156$ e Å^{-3}
$\Delta\rho_{\min} = -0.140$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.040 (5)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = −0.6 (13)

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

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

	x	y	z	$U_{\rm eq}$
O1	0.6152 (3)	0.2638 (2)	0.24865 (13)	0.0268 (5)
N2	0.7749 (4)	0.2306 (3)	0.1911 (2)	0.0267 (6)
C3	0.8436 (4)	0.3392 (3)	0.1580 (2)	0.0216 (6)
C4	0.7320 (4)	0.4642 (3)	0.1856 (2)	0.0246 (7)
C5	0.6329 (4)	0.4086 (3)	0.2658 (2)	0.0222 (7)
O1′	0.3176 (3)	0.6307 (2)	0.47376 (12)	0.0242 (5)
C2′	0.2500 (4)	0.5767 (3)	0.5555 (2)	0.0275 (7)
C3′	0.0410 (4)	0.6349 (4)	0.5774 (2)	0.0313 (8)
C4′	−0.1239 (5)	0.6126 (3)	0.4984 (2)	0.0284 (7)
C5′	−0.0446 (4)	0.6699 (3)	0.4140 (2)	0.0253 (7)
C6′	0.1710 (4)	0.6133 (3)	0.3980 (2)	0.0210 (6)
C7′	0.2762 (4)	0.6803 (3)	0.3206 (2)	0.0210 (6)
O8′	0.1192 (3)	0.6785 (2)	0.24653 (12)	0.0238 (5)
C9′	0.1806 (5)	0.7412 (3)	0.1669 (2)	0.0272 (7)
C10′	0.2416 (5)	0.8873 (3)	0.1840 (2)	0.0309 (7)
C11′	0.4220 (5)	0.8943 (3)	0.2577 (2)	0.0326 (8)
C12′	0.3582 (5)	0.8226 (3)	0.3416 (2)	0.0267 (7)
O13′	0.4562 (3)	0.6054 (2)	0.29861 (12)	0.0216 (5)
C14′	0.4180 (4)	0.4640 (3)	0.2819 (2)	0.0218 (6)
C15′	0.3252 (5)	0.4016 (3)	0.3611 (2)	0.0257 (7)
O16′	0.1368 (3)	0.4728 (2)	0.37938 (13)	0.0246 (5)
C1*P*	1.0131 (4)	0.3370 (3)	0.0972 (2)	0.0234 (7)
C2*P*	1.1602 (5)	0.2317 (3)	0.1015 (2)	0.0299 (7)
C3*P*	1.3217 (5)	0.2320 (4)	0.0451 (2)	0.0353 (8)
C4*P*	1.3399 (5)	0.3367 (4)	−0.0154 (2)	0.0379 (8)
C5*P*	1.1974 (5)	0.4425 (3)	−0.0192 (2)	0.0338 (8)
C6*P*	1.0355 (4)	0.4432 (3)	0.0374 (2)	0.0263 (7)

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

O1—N2	1.425 (3)	C6′—O16′	1.430 (4)
O1—C5	1.458 (4)	C6′—C7′	1.536 (4)
N2—C3	1.275 (4)	C7′—O8′	1.423 (3)
C3—C1*P*	1.469 (4)	C7′—O13′	1.425 (3)
C3—C4	1.501 (4)	C7′—C12′	1.524 (4)
C4—C5	1.506 (4)	O8′—C9′	1.425 (4)
C5—C14′	1.510 (4)	C9′—C10′	1.513 (5)
O1′—C6′	1.412 (3)	C10′—C11′	1.519 (4)
O1′—C2′	1.434 (3)	C11′—C12′	1.526 (4)
C2′—C3′	1.510 (4)	O13′—C14′	1.438 (4)
C3′—C4′	1.524 (4)	C14′—C15′	1.500 (4)
C4′—C5′	1.509 (4)	C15′—O16′	1.436 (4)
C5′—C6′	1.519 (4)	C1*P*—C6*P*	1.394 (4)
O1′—C6′—C7′—O8′	−172.9 (2)	O1—C5—C14′—C15′	60.5 (3)
O1—C5—C14′—O13′	179.5 (2)	N2—C3—C1*P*—C2*P*	−26.3 (4)

Table 3. *Puckering Parameters (Å, °)*

Ring†	Q	θ	φ
Isoxazoline (O1–N2–C3–C4–C5)	0.258 (3)	–	319.3 (5)
Dioxane (O13′–C14′–C15′–O16′–C6′–C7′)	0.534 (3)	175.4 (3)	57 (4)
Pyranoid (O1′–C6′–C5′–C4′–C3′–C2′)	0.544 (3)	176.5 (3)	28 (5)
Pyranoid (O8′–C7′–C12′–C11′–C10′–C9′)	0.547 (3)	173.3 (3)	64 (3)

† Numbered in order of calculation (Cremer & Pople, 1975).

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1176). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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