C6—C7—C8—C9	5.5 (3)	C16—C17—C20—C22	57.4 (3)
C7—C8—C9—C10	23.9 (2)	C20—C22—C23—C24	178.0 (3)
C8—C14—C13—C12	−59.7 (2)		

All non-H atoms were located by direct methods. All H atoms were found from difference Fourier maps. All non-H atoms were refined anisotropically and H atoms isotropically.

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1992). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1087). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(2′*S*,3′*S*,4′*R*)-5′-*O*-Benzoyl-3′-deoxy-3′β-diethylphosphono-2′-*O*-*tert*-butyldimethylsilyluridine

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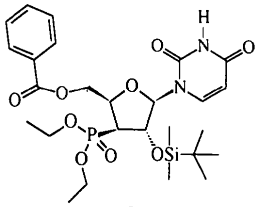
Abstract

3′-Hydroxy-3′-diethylphosphononucleosides readily undergo radical deoxygenation under modified Barton conditions to give two diastereomers of the parent diethyl phosphonate. However, the stereochemistry of the diastereomers is difficult to establish by spectral means. When the major product of one such reaction was obtained in crystalline form, a single crystal diffraction analysis was conducted on that diastereomer, the title compound, $C_{26}H_{39}N_2O_9PSi$.

Comment

A modified Barton deoxygenation protocol suitable for deoxygenation of tertiary alcohols was reported by Dolan & MacMillan in 1985, but there have been few applications of this methodology in carbohydrate or nucleoside systems (Matsusda, Takenuki, Sasaki & Ueda, 1991; Kakefuda, Yoshimura, Sasaki & Matsuda, 1993; Serra, Dewynter, Montero & Imbach, 1994). In all previous cases, the stereochemistry of the products was assigned by analysis of the NMR spectra. After deoxygenation of 5′-*O*-benzoyl-3′α-diethylphosphono-3′β-hydroxy-2′-*O*-*tert*-butyldimethylsilyluridine *via* this procedure (McEldoon & Wiemer, 1995), the 3′-stereochemistry of the title product, (I), was established by a single-crystal diffraction analysis.



(I)

The diffraction analysis revealed an intermolecular hydrogen bond between the H atom of N3 and the phosphoryl O atom [N3···O5^{i} 2.924 (7), H3···O5^{i} 2.17 (5) Å, N3—H3···O5^{i} 176 (5)°; symmetry code: (i) $x - 1/2, -y + 1/2, -z + 1$]. It also established that the ribose ring adopts an O4′,C4′ half-chair conformation. The conformation about the glycosidic bond is *anti* [O4′—C1—N1—C2 = 242.7 (5)°].

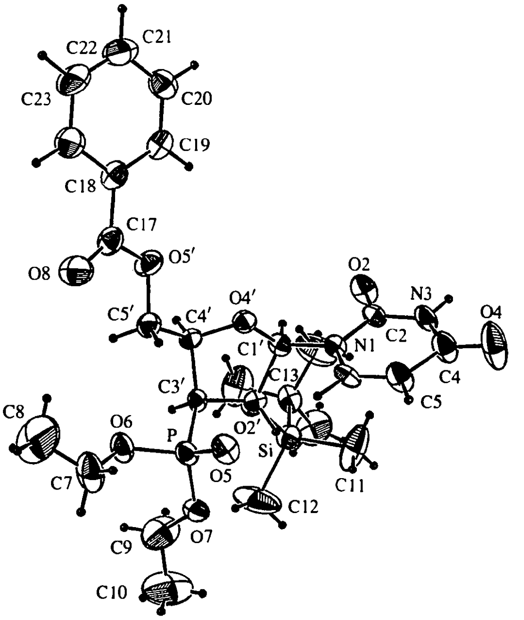


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. Displacement ellipsoids are plotted at the 35% probability level.

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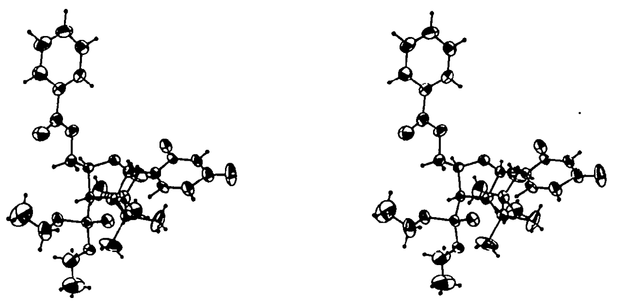

Fig. 2. An *ORTEP*II (Johnson, 1976) stereo drawing of the title compound. Displacement ellipsoids are plotted at the 35% probability level.

Experimental

Application of the radical deoxygenation protocol to 5′-*O*-benzoyl-3′α-diethylphosphono-3′β-hydroxy-2′-*O*-*tert*-butyldimethylsilyluridine afforded a 1.8:1 mixture of diastereomers (McEldoon & Wiemer, 1995). After separation of the diastereomeric products by radial chromatography ($CHCl_3$:MeOH, 95:5), the major isomer was dissolved in a minimum amount of ethyl alcohol at room temperature. The container was moved to a refrigerator, and allowed to stand at 277 K open to air for approximately 24 h. Clear needle-shaped crystals were then apparent, and no solvent remained.

Crystal data

$C_{26}H_{39}N_2O_9PSi$
M_r = 582.66
Orthorhombic
$P2_12_12_1$
a = 13.695 (4) Å
b = 25.34 (1) Å
c = 9.128 (3) Å
V = 3167 (3) Å^3
Z = 4
D_x = 1.22 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11–15°
μ = 0.167 mm^{-1}
T = 291 K
Needle
0.60 × 0.15 × 0.03 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4791 measured reflections
4042 independent reflections
2239 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int}$ = 0.051
$\theta_{\rm max}$ = 27.5°
$h = -17 \rightarrow 0$
$k = -1 \rightarrow 32$
$l = -11 \rightarrow 3$
4 standard reflections
frequency: 480 min
intensity decay: 0.86%

Refinement

Refinement on F
R = 0.051
wR = 0.053
S = 1.054
2239 reflections
356 parameters
H3 refined, all other H atoms positioned using a riding model with U(H) = 1.1U(bonded atom)

Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\rm max}$ = 0.041
$\Delta\rho_{\rm max}$ = 0.24 e Å^{-3}
$\Delta\rho_{\rm min}$ = 0.08 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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	$U_{\rm eq}$
P	0.5534 (1)	0.37815 (6)	0.8013 (2)	0.0441 (3)
Si	0.2364 (1)	0.30936 (7)	1.0008 (2)	0.0570 (4)
O4′	0.3786 (3)	0.3707 (1)	0.5332 (4)	0.047 (1)
O5	0.5939 (3)	0.3402 (2)	0.6969 (5)	0.055 (1)
O6	0.5987 (2)	0.4350 (1)	0.8025 (5)	0.057 (1)
O7	0.5626 (3)	0.3558 (1)	0.9614 (4)	0.059 (1)
O2′	0.2820 (3)	0.3509 (1)	0.8791 (4)	0.049 (1)
O2	0.1631 (2)	0.2804 (2)	0.5207 (5)	0.060 (1)
O4	0.3441 (3)	0.1402 (2)	0.3830 (8)	0.119 (2)
O5′	0.4285 (3)	0.4674 (2)	0.4115 (4)	0.059 (1)
O8	0.5629 (3)	0.5145 (2)	0.3702 (5)	0.081 (1)
N1	0.3275 (3)	0.2834 (2)	0.5625 (5)	0.038 (1)
N3	0.2565 (3)	0.2107 (2)	0.4554 (5)	0.053 (1)
C3′	0.4249 (3)	0.3929 (2)	0.7745 (6)	0.037 (1)
C2′	0.3608 (4)	0.3430 (2)	0.7826 (6)	0.038 (1)
C1′	0.3218 (4)	0.3365 (2)	0.6233 (6)	0.043 (1)
C4′	0.3985 (4)	0.4156 (2)	0.6216 (6)	0.041 (1)
C7	0.7022 (4)	0.4465 (3)	0.785 (1)	0.089 (3)
C8	0.7122 (6)	0.4991 (4)	0.731 (2)	0.221 (6)
C9	0.5526 (8)	0.3858 (3)	1.0903 (8)	0.121 (3)
C10	0.5887 (9)	0.3628 (4)	1.220 (1)	0.177 (4)
C11	0.2543 (6)	0.2407 (3)	0.938 (1)	0.121 (3)
C12	0.3025 (7)	0.3197 (5)	1.1764 (9)	0.150 (4)
C13	0.1062 (4)	0.3276 (2)	1.0159 (7)	0.058 (2)
C16	0.0563 (6)	0.2969 (4)	1.139 (1)	0.112 (3)
C15	0.0527 (6)	0.3170 (4)	0.876 (1)	0.123 (3)
C14	0.0952 (6)	0.3867 (3)	1.047 (1)	0.119 (3)
C2	0.2428 (3)	0.2596 (2)	0.5126 (6)	0.042 (1)
C4	0.3436 (4)	0.1832 (2)	0.4367 (8)	0.066 (2)
C5	0.4276 (4)	0.2124 (2)	0.4857 (7)	0.059 (2)
C6	0.4183 (4)	0.2600 (2)	0.5450 (6)	0.047 (2)
C5′	0.4721 (4)	0.4495 (2)	0.5472 (7)	0.053 (2)
C17	0.4849 (4)	0.4995 (2)	0.3308 (7)	0.055 (2)
C18	0.4374 (4)	0.5139 (2)	0.1906 (7)	0.052 (2)
C19	0.3548 (4)	0.4884 (2)	0.1379 (7)	0.053 (2)
C20	0.3151 (4)	0.5019 (2)	0.0052 (8)	0.064 (2)
C21	0.3557 (6)	0.5410 (3)	−0.0744 (8)	0.086 (2)
C22	0.4373 (6)	0.5668 (3)	−0.0259 (9)	0.108 (3)
C23	0.4777 (5)	0.5539 (3)	0.1078 (8)	0.080 (2)

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

P—O5	1.464 (4)	O4—C4	1.195 (7)
P—O6	1.568 (4)	O5′—C5′	1.449 (8)
P—O7	1.573 (5)	O5′—C17	1.342 (7)
P—C3′	1.816 (5)	O8—C17	1.190 (7)
Si—O2′	1.653 (4)	N1—C1′	1.457 (7)
Si—C11	1.847 (8)	N1—C2	1.385 (7)
Si—C12	1.859 (9)	N1—C6	1.387 (7)
Si—C13	1.847 (7)	N3—C2	1.356 (8)
O4′—C1′	1.425 (7)	N3—C4	1.392 (8)
O4′—C4′	1.421 (7)	N3—H3	0.76 (5)
O6—C7	1.455 (7)	C3′—C2′	1.541 (8)
O7—C9	1.408 (9)	C3′—C4′	1.552 (8)
O2′—C2′	1.407 (6)	C2′—C1′	1.558 (8)
O2—C2	1.215 (6)		
O5—P—O6	117.3 (3)	O4′—C4′—C5′	109.5 (5)
O5—P—O7	109.7 (3)	C3′—C4′—C5′	117.8 (5)
O5—P—C3′	114.5 (3)	O6—C7—C8	108.5 (7)
O6—P—O7	107.1 (3)	O7—C9—C10	116.3 (8)
O6—P—C3′	101.2 (2)	Si—C13—C16	111.0 (6)
O7—P—C3′	106.1 (3)	Si—C13—C15	111.3 (5)
O2′—Si—C11	109.9 (4)	Si—C13—C14	110.7 (5)
O2′—Si—C12	107.8 (3)	C16—C13—C15	108.6 (7)
O2′—Si—C13	104.8 (3)	C16—C13—C14	108.5 (7)
C11—Si—C12	109.6 (6)	C15—C13—C14	106.6 (8)
C11—Si—C13	112.7 (4)	O2—C2—N1	122.8 (6)
C12—Si—C13	111.8 (5)	O2—C2—N3	123.0 (5)
C1′—O4′—C4′	105.3 (4)	N1—C2—N3	114.2 (5)
P—O6—C7	124.6 (4)	O4—C4—N3	120.7 (6)

P—O7—C9	125.0 (5)	O4—C4—C5	126.3 (6)
Si—O2′—C2′	128.3 (4)	N3—C4—C5	113.0 (6)
C5′—O5′—C17	114.9 (5)	C4—C5—C6	121.1 (6)
C1′—N1—C2	118.9 (5)	N1—C6—C5	121.4 (5)
C1′—N1—C6	119.1 (5)	O5′—C5′—C4′	106.9 (5)
C2—N1—C6	121.7 (5)	O5′—C17—O8	123.0 (7)
C2—N3—C4	128.4 (5)	O5′—C17—C18	111.8 (6)
P—C3′—C2′	112.1 (4)	O8—C17—C18	125.3 (6)
P—C3′—C4′	115.1 (4)	C17—C18—C19	122.9 (6)
C2′—C3′—C4′	102.4 (4)	C17—C18—C23	118.6 (6)
O2′—C2′—C3′	110.5 (4)	C19—C18—C23	118.5 (6)
O2′—C2′—C1′	109.6 (4)	C18—C19—C20	120.9 (6)
C3′—C2′—C1′	103.7 (5)	C19—C20—C21	119.7 (7)
O4′—C1′—N1	108.2 (4)	C20—C21—C22	120.9 (8)
O4′—C1′—C2′	106.7 (4)	C21—C22—C23	120.1 (8)
N1—C1′—C2′	115.8 (5)	C18—C23—C22	119.9 (7)
O4′—C4′—C3′	105.0 (4)		
C4′—O4′—C1′—C2′	−35.1 (5)	C2′—C3′—C4′—O4′	−32.7 (5)
C1′—O4′—C4′—C3′	42.7 (5)	C3′—C2′—C1′—O4′	13.3 (5)
C4′—C3′—C2′—C1′	11.2 (5)		

The diffraction analysis clearly demonstrates that the crystalline product is the 3′β-diethylphosphono isomer, indicating that H-atom transfer has occurred primarily to the less hindered α face in this product. The major product is formed with inversion of the C3′ stereochemistry. The structure was determined by direct methods. The absolute stereochemistry of the ribose moiety was known in advance so no attempt was made to determine the absolute configuration from X-ray diffraction data. The scattering factors f' and f'' were included in the structure-factor calculations.

Data collection: Enraf–Nonius (1977) CAD-4 software. Cell refinement: Enraf–Nonius (1977) CAD-4 software. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN* (Main *et al.*, 1980). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF VAX* in *MolEN*.

Financial support from the National Institutes of Health (GM-44986) is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SX1005). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,3-Dicyclohexyl-2,4-bis(cyclohexylimino)-1,3-diazetidine: Dimer of Dicyclohexylcarbodiimide

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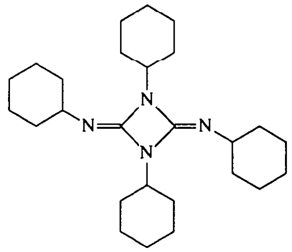
Abstract

The title compound, $C_{26}H_{44}N_4$, was isolated as a by-product of an esterification reaction using dicyclohexylcarbodiimide as a dehydrating agent. The X-ray structure determination reveals a highly symmetrical molecule with a non-crystallographic inversion centre as a symmetry element. The substituents of the azetidine ring are cyclohexane rings with ideal chair conformation.

Comment

During our attempts to determine the enantiomeric excess and the absolute configuration of several optically active fluorohydrins by derivatization with enantiopure carboxylic acids, we used the DCC method (DCC = dicyclohexylcarbodiimide) recommended for this type of esterification (Heumann & Faure, 1993). However, some of these reactions failed and we obtained the dimer of DCC. This compound, (I), had been found earlier as a major by-product in peptide synthesis with DCC and 1-hydroxybenzotriazole (Jakubke & Klessen, 1977) and can be synthesized by the reaction of DCC with SO_2 gas at 273 K for 21 h (Kaupp, Luebben & Sauerland, 1990).



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