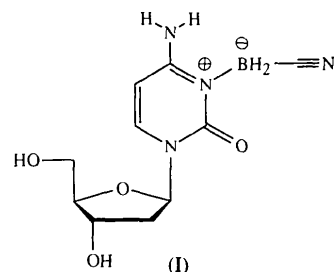


- Killean, R. C. G. & Lawrence, J. L. (1969). *Acta Cryst.* **B25**, 1750–1752.
- Lilley, T. H. (1988). *Biochemical Thermodynamics*, edited by M. N. Jones, pp. 1–52. Amsterdam: Elsevier.
- Milburn, P. J. (1984). PhD thesis, University of Sheffield, England.
- Puliti, R., Barone, G., Giancola, C. & Mattia, C. A. (1996). *J. Mol. Struct.* In the press.
- Puliti, R. & Mattia, C. A. (1995). *Acta Cryst.* **C51**, 336–339.
- Ramachandran, G. N., Kolaskar, A. S., Ramakrishnan, C. & Sasisekharan, V. (1974). *Biochim. Biophys. Acta*, **359**, 298–302.
- Stout, G. H. & Jensen, L. H. (1968). *X-ray Structure Determination*, pp. 409–412. New York: Macmillan.
- Vásquez, M., Némethy, G. & Scheraga, H. A. (1983). *Macromolecules*, **16**, 1043–1049.
- Zimmerman, S. S., Pottle, M. S., Némethy, G. & Scheraga, H. A. (1977). *Macromolecules*, **10**, 1–9.



The cytosine ring is planar with the following deviations from the best least-squares plane, N1 -0.015 (2), C2 0.021 (2), N3 -0.009 (2), C4 -0.008 (2), C5 0.015 (3), C6 -0.003 (2) Å. The non-H substituents deviate significantly from the plane with C1' out-of-plane by -0.155 (2), O2 by 0.029 (2), B31 by -0.102 (3) and N4 by -0.034 (2) Å. The torsion angles for the cytosine ring, ranging from 0.4 (3) to 3.7 (3)°, are in good agreement with the typical value obtained by Taylor & Kennard (1982) for a pyrimidine ring.

Unlike the $P2_1$ form, the furanose ring in the $P2_12_12_1$ form is in an envelope conformation with C2' deviating 0.523 (3) Å from the plane containing the other four atoms and the 2E puckering mode is assumed. The angle of pseudorotation P is -13.2° and v_{\max} is 18.8° (Saenger, 1984). In addition, the torsion angles C3'—C4'—C5'—O5' 66.4 (3)° and O4'—C4'—C5'—O5' -176.0 (2)°, demonstrate that the conformation around the exocyclic bond, C4'—C5', is *tg*.

However, the torsion angle O4'—C1'—N1—C6 -14.6 (3)°, shows that the glycosyl conformation remains *anti*.

In the crystal, as shown in Fig. 2 and Table 2, molecules are linked through hydrogen bonds between bases, C5—H···O2 and N4—H···O2, to form infinite long chains along the b axis. These long chains are crosslinked by hydrogen bonds from sugar to sugar and from sugar to base, O5'—H···O3' and O3'—H···N31, resulting in total in a three-dimensional hydrogen-bond network.

Acta Cryst. (1996). **C52**, 1823–1825

2'-Deoxycytidine-N3-cyanoborane

QI GAO,^a ANUP SOOD,^b BARBARA RAMSAY SHAW^b AND LOREN D. WILLIAMS^c

^aAnalytical Research and Development, Pharmaceutical Research Institute, Bristol-Myers Squibb Company, 5 Research Parkway, Wallingford, CT 06492-7660, USA,

^bPaul Gross Laboratory, Department of Chemistry, Duke University, Durham, NC 27706, USA, and ^cSchool of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, USA

(Received 16 May 1995; accepted 6 October 1995)

Abstract

The structure of the $P2_12_12_1$ form of 2'-deoxycytidine-N3-cyanoborane, $C_{10}H_{15}BN_4O_4$, has been determined. The sugar is in the 2E puckering mode and the C5'—O5' bond has a *tg* conformation while the relative orientation of the sugar and the base remains *anti*.

Comment

The bond lengths and angles of the title molecule, (I), in the $P2_12_12_1$ form described here are similar to those in the $P2_1$ form (Singh, Zottola, Ramsay Shaw & Pedersen, 1996). In the $P2_12_12_1$ form, the B atom is tetrahedral with bond angles ranging from 107.5 (2) to 110.1 (2)°. The B—C≡N moiety has a bent geometry as indicated by the angle 176.0 (3)°. Consistent with the $P2_1$ form, the exocyclic bond angle C4—N3—B, 124.3 (2)°, is larger than C2—N3—B, 115.5 (2)°. One of the BH₂ H atoms is in close van der Waals contact with one of the NH₂ H atoms (1.944 Å).

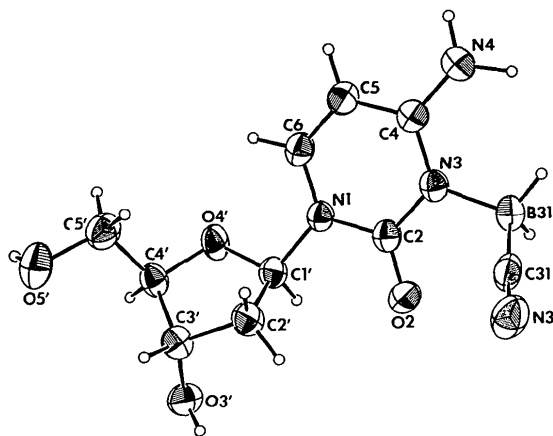


Fig. 1. Molecular structure of the title compound with displacement ellipsoids plotted at the 50% probability level.

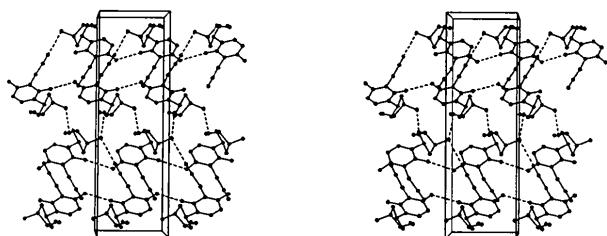


Fig. 2. Stereoview of the unit cell of 2'-deoxycytidine-N3-cyanoborane.

O5'	1.3160 (3)	0.95464 (9)	0.0911 (3)	4.14 (4)
N1	0.6653 (3)	0.89261 (9)	0.0731 (3)	2.56 (4)
N3	0.4524 (3)	0.82252 (9)	0.0006 (3)	2.53 (4)
N4	0.3822 (3)	0.8073 (1)	-0.3198 (4)	3.84 (5)
N31	0.4967 (3)	0.6800 (1)	0.2610 (5)	4.22 (5)
C1'	0.7777 (3)	0.9175 (1)	0.2227 (4)	2.79 (5)
C2'	0.9018 (4)	0.8706 (1)	0.2914 (4)	3.11 (5)
C2	0.5471 (3)	0.8524 (1)	0.1363 (4)	2.64 (5)
C3'	1.0462 (3)	0.9100 (1)	0.3480 (4)	2.81 (5)
C4'	1.0388 (3)	0.9628 (1)	0.2063 (4)	2.84 (5)
C4	0.4721 (3)	0.8354 (1)	-0.1904 (4)	2.70 (5)
C5'	1.1499 (4)	0.9536 (1)	0.0346 (4)	3.69 (4)
C5	0.5893 (4)	0.8788 (1)	-0.2476 (4)	3.03 (5)
C6	0.6838 (3)	0.9058 (1)	-0.1167 (4)	2.93 (5)
C31	0.4306 (3)	0.7205 (1)	0.1881 (4)	3.12 (5)
B31	0.3313 (4)	0.7727 (1)	0.0812 (1)	3.01 (6)

Experimental

Recrystallization from hot water gave colorless rods.

Crystal data

C₁₀H₁₅BN₄O₄

M_r = 266.05

Orthorhombic

*P*2₁2₁2₁

a = 8.144 (1) Å

b = 21.772 (1) Å

c = 6.966 (1) Å

V = 1235.2 (2) Å³

Z = 4

D_x = 1.430 Mg m⁻³

Cu *K*α radiation

λ = 1.5418 Å

Cell parameters from 25 reflections

θ = 14.90–24.76°

μ = 0.883 mm⁻¹

T = 295 K

Rod

0.40 × 0.20 × 0.15 mm

Colorless

Data collection

Rigaku AFC-5 diffractometer

ω scans

Absorption correction:

empirical, ψ scan (North, Phillips & Mathews, 1968)

T_{min} = 0.84, *T_{max}* = 0.99

2045 measured reflections

1119 independent reflections

1024 observed reflections

[*F* ≥ 3σ(*F*)]

R_{int} = 0.017

θ_{max} = 60°

h = 0 → 9

k = 0 → 24

l = -7 → 7

3 standard reflections

monitored every 150

reflections

intensity decay: <4%

Refinement

Refinement on *F*²

R = 0.029

wR = 0.042

S = 1.505

1024 reflections

173 parameters

H-atom parameters not

refined

w = 1/σ²

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.115 e Å⁻³

Δρ_{min} = -0.132 e Å⁻³

Extinction correction:

F_c^{*} = *F_c*(1 + *gI_c*)⁻¹

Extinction coefficient:

1.752 × 10⁻⁵

Atomic scattering factors

from *MolEN* (Fair, 1990)

Table 2. Selected geometric parameters (Å, °)

O2—C2	1.225 (3)	N3—B31	1.570 (4)
O3'—C3'	1.430 (3)	N4—C4	1.313 (4)
O4'—C1'	1.411 (3)	N31—C31	1.150 (4)
O4'—C4'	1.455 (3)	C1'—C2'	1.514 (4)
O5'—C5'	1.410 (4)	C2'—C3'	1.509 (4)
N1—C1'	1.490 (3)	C3'—C4'	1.516 (4)
N1—C2	1.374 (3)	C4'—C5'	1.513 (4)
N1—C6	1.361 (4)	C4—C5	1.400 (4)
N3—C2	1.383 (3)	C5—C6	1.331 (4)
N3—C4	1.369 (4)	C31—B31	1.582 (4)
C1'—O4'—C4'	109.9 (2)	O3'—C3'—C2'	111.6 (2)
C1'—N1—C2	116.0 (2)	O3'—C3'—C4'	108.9 (2)
C1'—N1—C6	122.3 (2)	C2'—C3'—C4'	103.3 (2)
C2—N1—C6	121.5 (2)	O4'—C4'—C3'	106.0 (2)
C2—N3—C4	120.1 (2)	O4'—C4'—C5'	109.0 (2)
C2—N3—B31	115.5 (2)	C3'—C4'—C5'	113.0 (2)
C4—N3—B31	124.3 (2)	N3—C4—N4	120.4 (2)
O4'—C1'—N1	108.3 (2)	N3—C4—C5	119.7 (2)
O4'—C1'—C2'	106.2 (2)	N4—C4—C5	120.0 (3)
N1—C1'—C2'	112.6 (2)	O5'—C5'—C4'	110.6 (2)
C1'—C2'—C3'	102.6 (2)	C4—C5—C6	119.8 (3)
O2—C2—N1	120.4 (2)	N1—C6—C5	120.6 (2)
O2—C2—N3	121.4 (2)	N31—C31—B31	176.0 (3)
N1—C2—N3	118.1 (2)	N3—B31—C31	110.1 (2)
C4'—O4'—C1'—N1	139.5 (2)	C2—N1—C1'—C2'	-73.7 (3)
C1'—O4'—C4'—C3'	3.3 (3)	C6—N1—C1'—C2'	102.5 (3)
C2—N1—C1'—O4'	169.2 (2)	C1'—N1—C2—N3	172.5 (2)
C6—N1—C1'—O4'	-14.6 (3)	C6—N1—C2—N3	-3.7 (3)
C1'—N1—C2—O2	-4.8 (3)	C2—N1—C6—C5	1.5 (4)
C6—N1—C2—O2	178.9 (2)	C4—N3—C2—N1	3.1 (3)
C1'—N1—C6—C5	-174.5 (2)	B31—N3—C2—N1	-174.5 (2)
C4—N3—C2—O2	-179.6 (2)	C2—N3—C4—C5	-0.4 (3)
B31—N3—C2—O2	2.8 (3)	B31—N3—C4—C5	177.0 (2)
C2—N3—C4—N4	179.9 (2)	C4—N3—B31—C31	-116.9 (3)
B31—N3—C4—N4	-2.8 (4)	N1—C1'—C2'—C3'	-150.7 (2)
C2—N3—B31—C31	60.5 (3)	C1'—C2'—C3'—C4'	33.3 (3)
O4'—C1'—C2'—C3'	-32.3 (3)	O3'—C3'—C4'—C5'	-145.2 (2)
C1'—C2'—C3'—O3'	-83.6 (2)	C2'—C3'—C4'—C5'	96.0 (3)
O3'—C3'—C4'—O4'	95.4 (2)	C3'—C4'—C5'—O5'	66.4 (3)
C2'—C3'—C4'—O4'	-23.3 (3)	N3—C4—C5—C6	-1.9 (4)
O4'—C4'—C5'—O5'	-176.0 (2)	C4—C5—C6—N1	1.3 (4)
C4'—O4'—C1'—C2'	18.3 (3)	N4—C4—C5—C6	177.8 (2)
C1'—O4'—C4'—C5'	-118.6 (2)	N31—C31—B31—N3	139.6 (4)
N4...O2'	2.959 (4)	O5...O3''	2.766 (4)
C5...O2'	3.232 (4)	C3...N31'''	2.858 (4)

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

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

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
O2	0.5312 (3)	0.84191 (9)	0.3081 (3)	3.71 (4)
O3'	1.0279 (3)	0.93380 (8)	0.5380 (3)	3.55 (4)
O4'	0.8693 (2)	0.96586 (7)	0.1409 (3)	3.25 (4)

The structure was solved by direct methods and was refined by full-matrix least-squares techniques using *MolEN* (Fair, 1990). Although all H atoms were observed in difference Fourier maps, only the two hydroxyl H atoms in the molecule were located experimentally and the positions of all the other H atoms were calculated from an idealized geometry with standard bond lengths and angles.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1158). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 Saenger, W. (1984). *Principles of Nucleic Acid Structure*, pp. 17–21. New York: Springer-Verlag.
 Singh, P., Zottola, M., Ramsay Shaw, B. & Pedersen, L. G. (1996). *Acta Cryst.* **C52**, 693–696.
 Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 3209–3212.

Acta Cryst. (1996). **C52**, 1825–1826

5,6,7,8,9,10-Hexahydro-10-hydroxy-5,9-methano-4H-thieno[3,2-c]azonine

JOZEF KOŽIŠEK,^{a*} DUŠAN BERKEŠ,^b INGRID SVOBODA^c AND BERNARD DECROIX^d

^aDepartment of Inorganic Chemistry, Faculty of Chemical Technology, Radlinského 9, Slovak Technical University, 812 37 Bratislava, Slovakia, ^bDepartment of Organic Chemistry, Faculty of Chemical Technology, Radlinského 9, Slovak Technical University, 812 37 Bratislava, Slovakia, ^cFachbereich Materialwissenschaft, Technische Hochschule Darmstadt, Petersenstrasse 20, D-642 87 Darmstadt, Germany, and ^dLaboratoire de Chimie, Université Le Havre, 30 Rue Gabriel Péri, 766 00 Le Havre, France. E-mail: kozisek@cvstst.u.cvststuba.sk

(Received 4 October 1995; accepted 21 February 1996)

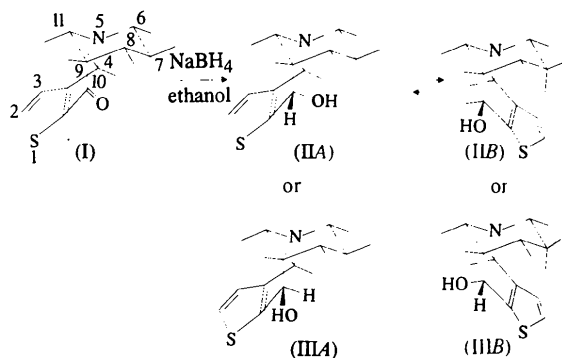
Abstract

The title molecule, C₁₁H₁₅NOS, consists of a seven-membered azepine ring fused to both a five-membered thiophene ring and a six-membered piperidine ring so that a methylene bridge links positions 5 and 9. The thiophene ring is planar, while the azepine ring adopts a pseudo-chair conformation with a pseudo-equatorial hydroxy group at C10. The 1,3-fused piperidine ring also possesses a chair conformation.

Comment

The observation that bridged benzo-fused azocines were obtained in the course of the synthesis of novel non-competitive antagonists of *N*-methyl-D-aspartic acid (NMDA) (Blough, Mascarella, Rothman & Carroll, 1993) stimulated us to search for thieno analogues of this system together with its homologues (Berkeš &

Decroix, 1994; Berkeš, Bar & Decroix, 1995). The stereoselective reduction of 5,6,7,8,9,10-hexahydro-5,9-methano-4H-thieno[3,2-c]azonin-10-one, (I), with NaBH₄ in ethanol at 298 K led to the title compound (II) (Berkeš, Bar & Decroix, 1995). Only one diastereomer was isolated and its structure was inferred from exhaustive ¹H and ¹³C NMR studies.



The X-ray analysis was undertaken in order to distinguish between the diastereomer (II) and possible diastereomer (III), which differ in their relative configurations at the second newly formed asymmetric C10 centres. The other reason was to distinguish between the relative configurations *R**,*R** and *R**,*S**; the *R**,*R** relative configuration is associated with the pseudo-chair conformation of the seven-membered ring found in structure (IIA), whereas a twisted conformation of the seven-membered ring occurs in the *R**,*S** structure (IIIA). The piperidine ring in all cases has a chair conformation. The results establish that diastereomer (II) is formed in preference to (III) and that the conformation is that of (IIB) in which the seven-membered azepine ring is in the chair form (Fig. 1).

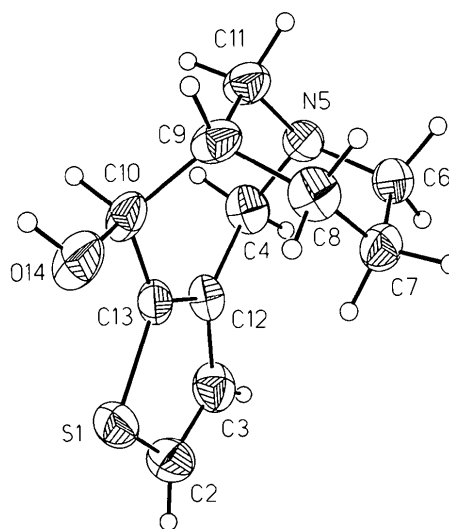


Fig. 1. The molecular structure of the title compound, with displacement ellipsoids given at 50% probability and H atoms shown as spheres of arbitrary radii.