

- Buchi, G., Francisco, M. A., Murray, W. V., Kachholz, T., Demain, A. L. & Blount, J. F. (1983). *Tetrahedron Lett.* **24**, 2527–2530.
- Decosterd, L. A., Stoeckli-Evans, H., Chapuis, J.-C., Sordat, B. & Hostettmann, K. (1989). *Helv. Chim. Acta*, **72**, 1833–1845.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.
- Fischer, N. H., Tanrisever, N. & Williamson, G. B. (1988). *Biologically Active Natural Products: Potential Use in Agriculture*, edited by H. G. Cutler, ACS Symposium Series No. 380, pp. 233–249. Washington, DC: American Chemical Society.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- Matsumoto, S., Matsuo, M. & Iitaka, Y. (1986). *J. Org. Chem.* **51**, 1435–1440.
- Obara, H., Onodera, J., Yusa, K., Tsuchiya, M. & Matsuba, S. (1989). *Bull. Chem. Soc. Jpn.* **62**, 3371–3372.
- Tanrisever, N., Fronczek, F. R., Fischer, N. H. & Williamson, G. B. (1987). *Phytochemistry*, **26**, 175–179.

Acta Cryst. (1993). **C49**, 1992–1994

Enantioselective Synthesis of Isoquinoline Alkaloids from Simple Sugar. I. Structure of an Oxaziridine Derivative

ZBIGNIEW CZARNOCKI

Department of Chemistry, Warsaw University,
Pasteura 1, 02-093 Warsaw, Poland

JAN K. MAURIN*

Institute of Atomic Energy, Solid State Physics
Department, 05-400 Otwock-Swierk, Poland

(Received 25 January 1993; accepted 4 May 1993)

Abstract

1-(6,7-Dimethoxy-1,2,3,4-tetrahydro-1,2-epoxyisoquinolin-1-yl)-1,2,3,4-butanetetrayl tetraacetate is a chiral precursor in the synthesis of some natural products. The three-membered oxaziridine ring is almost perpendicular to the best plane of the two remaining rings. The structure of the acetyl fragment is partly disordered.

Comment

In the course of our study on the enantioselective synthesis of isoquinoline alkaloids from various

naturally occurring chiral substrates, we launched a project using a simple sugar, D-ribonolactone (Bhat, Chen & Joullie, 1985, 1989), as a chiral building block. As a result of synthesis *via* several steps, we obtained two isoquinoline alkaloids: (*R*)-calycotomine and (*S*)-xylopinine (Czarnocki, 1992*a,b*). The oxaziridine derivative was obtained as one of many intermediate products. Its chemical reactivity will be the subject of a separate study. The compound was characterized by ^1H and ^{13}C NMR and its structure was established with some degree of certainty. However, the relative stereochemistry of the oxaziridine ring could not be established firmly by these methods. For this reason we decided to elucidate the proposed structure *via* an X-ray crystallographic study.

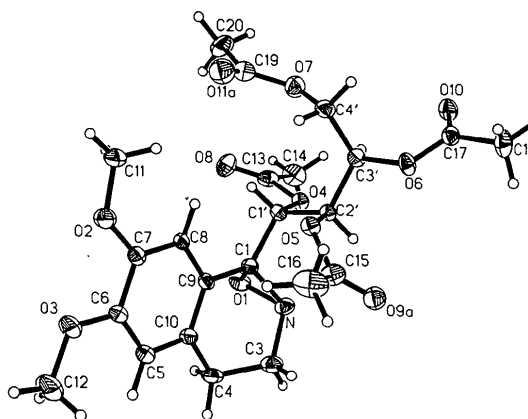


Fig. 1. Molecular geometry of the oxaziridine derivative.

The molecular geometry and numbering scheme are shown in Fig. 1. Only one position for each disordered acetyl O atom, O9 and O11, is shown in the figure for clarity. The refined site occupancies of the O9 atom were 0.48 (1) and 0.52 (1) for the *a* and *b* positions, respectively, whereas those of the O11 atom were 0.49 (2) and 0.51 (2), respectively. All bond lengths and angles are reasonable within experimental error. The aromatic ring (C5–C10) is planar. The C1–C9 and C6–O3 bonds are in the plane of the ring [angles with the normal to the plane are 89.7 (2) and 90.6 (2)°, respectively], whereas the two remaining bonds, C4–C10 and C7–O2, are slightly out of the plane [angles with the normal to the plane are 88.0 (3) and 91.6 (3)°, respectively]. The oxaziridine three-membered ring is almost perpendicular to the best plane defined by atoms of the two other rings [the dihedral angle is 91.8 (2)°]. The relative conformations on the C1 and C1' atoms, as shown in Fig. 1, were characterized by a series of torsion angles.

The formation of only one diastereoisomer of an oxaziridine derivative during synthesis (Czarnocki, 1992*a,b*) is noteworthy and indicates the highly stereospecific character of the oxidation step. This observation may be of great significance and we plan to utilize this compound as a chiral precursor in the synthesis of natural products.

Experimental

Crystal data

C₂₃H₂₉NO₁₁

$M_r = 495.482$

Orthorhombic

$P2_12_12_1$

$a = 19.482 (2) \text{ \AA}$

$b = 11.8207 (7) \text{ \AA}$

$c = 11.0553 (8) \text{ \AA}$

$V = 2545.9 (4) \text{ \AA}^3$

$Z = 4$

$D_x = 1.2927 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation

$\lambda = 1.54051 \text{ \AA}$

Data collection

Kuma Diffraction KM-4

diffractometer

ω - θ scans

Absorption correction:
none

2206 measured reflections

1857 independent reflections

1897 observed reflections

$[F > 3.92\sigma(F)]$

Refinement

Refinement on F^2

Final $R = 0.0589$

$wR = 0.0828$

$S = 3.30$

1857 reflections

315 parameters

Only common isotropic displacement parameter for H atoms refined

Cell parameters from 25 reflections

$\theta = 12-13.5^\circ$

$\mu = 0.8396 \text{ mm}^{-1}$

$T = 295 (2) \text{ K}$

Prismatic

$0.50 \times 0.30 \times 0.30 \text{ mm}$

Colorless

Crystal source: synthesis
(Czarnocki, 1992*a,b*);

crystallization from
chloroform solution by
slow evaporation

$R_{\text{int}} = 0.014$

$\theta_{\text{max}} = 60^\circ$

$h = 0 \rightarrow 18$

$k = -7 \rightarrow 0$

$l = -24 \rightarrow 24$

3 standard reflections

intensity variation: none

$w = 1/[\sigma(F) + 0.0005F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.033$

$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$

Extinction correction: none

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

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Program used for geometrical calculations: *PARST* (Nardelli, 1983). Molecular graphics: *ORTEPII* (Johnson, 1976).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$U_{\text{eq}} = 1/3(\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$				
	x	y	z	U_{eq}
N	0.5842 (2)	0.0138 (3)	0.4903 (4)	0.054 (1)
O1	0.5348 (2)	0.0356 (3)	0.5947 (3)	0.059 (1)
O2	0.6566 (2)	0.4856 (3)	0.7023 (4)	0.066 (1)

O3	0.7531 (2)	0.3809 (3)	0.8122 (4)	0.079 (1)
O4	0.4620 (1)	0.1161 (2)	0.4150 (3)	0.043 (1)
O5	0.6143 (2)	0.2735 (3)	0.3352 (3)	0.045 (1)
O6	0.5438 (2)	0.2677 (3)	0.1175 (3)	0.054 (1)
O7	0.4239 (2)	0.3792 (3)	0.3311 (3)	0.069 (1)
O8	0.4060 (2)	0.1896 (4)	0.5739 (4)	0.073 (1)
O9a	0.6797 (5)	0.1450 (7)	0.2395 (11)	0.069 (2)
O9b	0.6846 (4)	0.1290 (6)	0.2957 (10)	0.069 (2)
O10	0.4450 (2)	0.2428 (3)	0.0192 (3)	0.062 (1)
O11a	0.4638 (6)	0.5168 (13)	0.4475 (14)	0.089 (2)
O11b	0.4687 (5)	0.4790 (14)	0.4827 (13)	0.089 (2)
C1	0.5671 (2)	0.1269 (4)	0.5321 (4)	0.042 (1)
C3	0.6496 (3)	-0.0328 (4)	0.5376 (5)	0.064 (2)
C4	0.6697 (3)	0.0095 (4)	0.6629 (5)	0.060 (2)
C5	0.7152 (3)	0.1968 (5)	0.7365 (4)	0.054 (2)
C6	0.7102 (2)	0.3140 (4)	0.7449 (4)	0.051 (1)
C7	0.6573 (2)	0.3713 (4)	0.6846 (4)	0.046 (1)
C8	0.6124 (2)	0.3119 (3)	0.6139 (4)	0.039 (1)
C9	0.6166 (2)	0.1937 (4)	0.6059 (3)	0.040 (1)
C10	0.6676 (2)	0.1355 (4)	0.6674 (4)	0.049 (1)
C1'	0.5199 (2)	0.1868 (3)	0.4414 (4)	0.039 (1)
C2'	0.5536 (2)	0.2052 (3)	0.3185 (4)	0.038 (1)
C3'	0.5071 (2)	0.2642 (4)	0.2308 (4)	0.046 (1)
C4'	0.4872 (3)	0.3845 (4)	0.2604 (5)	0.058 (2)
C11	0.5974 (3)	0.5450 (4)	0.6621 (5)	0.068 (2)
C12	0.8062 (4)	0.3279 (8)	0.8734 (9)	0.126 (4)
C13	0.4083 (2)	0.1249 (4)	0.4934 (5)	0.055 (2)
C14	0.3550 (3)	0.0385 (6)	0.4592 (6)	0.075 (2)
C15	0.6754 (3)	0.2280 (4)	0.3038 (6)	0.067 (2)
C16	0.7317 (3)	0.3129 (7)	0.3223 (9)	0.101 (3)
C17	0.5048 (3)	0.2560 (4)	0.0178 (4)	0.050 (2)
C18	0.5479 (4)	0.2646 (6)	-0.0949 (4)	0.079 (2)
C19	0.4197 (3)	0.4478 (5)	0.4257 (6)	0.073 (2)
C20	0.3506 (4)	0.4441 (7)	0.4851 (7)	0.091 (3)

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

N—O1	1.523 (6)	O11a—C19	1.209 (15)
N—C1	1.452 (6)	O11b—C19	1.202 (13)
N—C3	1.484 (7)	C1—C9	1.491 (6)
O1—C1	1.427 (5)	C1—C1'	1.534 (6)
O2—C7	1.365 (5)	C3—C4	1.524 (8)
O2—C11	1.420 (7)	C4—C10	1.490 (7)
O3—C6	1.370 (6)	C5—C6	1.393 (7)
O3—C12	1.387 (10)	C5—C10	1.402 (7)
O4—C1'	1.434 (5)	C6—C7	1.401 (7)
O4—C13	1.363 (6)	C7—C8	1.368 (6)
O5—C2'	1.443 (5)	C8—C9	1.403 (6)
O5—C15	1.351 (6)	C9—C10	1.387 (6)
O6—C3'	1.443 (5)	C1'—C2'	1.525 (6)
O6—C17	1.346 (6)	C2'—C3'	1.500 (6)
O7—C4'	1.461 (6)	C3'—C4'	1.509 (7)
O7—C19	1.326 (7)	C13—C14	1.504 (8)
O8—C13	1.175 (7)	C15—C16	1.501 (9)
O9a—C15	1.214 (11)	C17—C18	1.506 (7)
O9b—C15	1.187 (9)	C19—C20	1.498 (10)
O10—C17	1.174 (7)		
O1—N—C1	57.2 (3)	C4—C10—C5	121.1 (4)
O1—N—C3	109.8 (4)	C4—C10—C9	119.9 (4)
C1—N—C3	115.2 (4)	C5—C10—C9	119.0 (4)
N—O1—C1	58.9 (3)	O4—C1'—C1	109.6 (3)
C7—O2—C11	116.9 (4)	O4—C1'—C2'	103.9 (3)
C6—O3—C12	117.4 (5)	C1—C1'—C2'	113.0 (3)
C1'—O4—C13	115.4 (3)	O5—C2'—C1'	108.6 (3)
C2'—O5—C15	117.8 (3)	O5—C2'—C3'	108.5 (3)
C3'—O6—C17	115.3 (4)	C1'—C2'—C3'	112.5 (3)
C4'—O7—C19	116.6 (4)	O6—C3'—C2'	105.9 (3)
N—C1—O1	63.9 (3)	O6—C3'—C4'	106.8 (4)
N—C1—C9	120.9 (4)	C2'—C3'—C4'	117.0 (4)
O1—C1—C9	114.9 (3)	O7—C4'—C3'	107.0 (4)
N—C1—C1'	110.8 (3)	O4—C13—O8	124.2 (5)
O1—C1—C1'	113.7 (4)	O4—C13—C14	108.5 (4)
C9—C1—C1'	120.1 (4)	O8—C13—C14	127.3 (5)
N—C3—C4	114.7 (4)	O5—C15—O9a	122.2 (6)
C3—C4—C10	110.6 (4)	O5—C15—O9b	123.1 (6)
C6—C5—C10	120.3 (5)	O5—C15—C16	110.0 (5)
O3—C6—C5	124.6 (4)	O9a—C15—C16	124.7 (7)

O3—C6—C7	115.3 (4)	O9b—C15—C16	124.0 (6)
C5—C6—C7	120.0 (4)	O6—C17—O10	124.3 (4)
O2—C7—C6	114.7 (4)	O6—C17—C18	110.8 (5)
O2—C7—C8	125.7 (4)	O10—C17—C18	124.9 (5)
C6—C7—C8	119.6 (4)	O7—C19—O11a	121.7 (9)
C7—C8—C9	120.7 (4)	O7—C19—O11b	123.5 (8)
C1—C9—C8	121.6 (4)	O7—C19—C20	112.6 (5)
C1—C9—C10	118.0 (4)	O11a—C19—C20	124.8 (9)
C8—C9—C10	120.4 (4)	O11b—C19—C20	119.5 (8)
N—C1—C1'—O4	52.2 (4)	O1—C1—C1'—C2'	-132.8 (4)
O1—C1—C1'—O4	-17.4 (5)	N—C1—C1'—C2'	-63.1 (5)
C9—C1—C1'—O4	-159.2 (3)	C9—C1—C1'—H1'	-35.3 (6)
O1—C1—C1'—H1'	106.5 (5)	C9—C1—C1'—C2'	85.4 (5)
N—C1—C1'—H1'	176.1 (4)		

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71301 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0308]

References

- Bhat, K. L., Chen, S.-Y. & Joullie, M. (1985). *Heterocycles*, **23**, 691–734.
- Bhat, K. L., Chen, S.-Y. & Joullie, M. (1989). *Aldrichimica Acta*, **22**(2), 49.
- Czarnocki, Z. (1992a). *J. Chem. Res. (S)*, pp. 334–335.
- Czarnocki, Z. (1992b). *J. Chem. Res. (M)*, pp. 2801–2819.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
- Sheldrick, G. M. (1990). *Acta Cryst. A* **46**, 467–473.

Acta Cryst. (1993). **C49**, 1994–1996

Structure of Tetraethylammonium Bromide–Succinimide (1/2)

MARGARETA ELDING-PONTÉN

Inorganic Chemistry 2, Chemical Center, University of Lund, PO Box 124, S-221 00 Lund, Sweden

(Received 13 January 1993; accepted 6 May 1993)

Abstract

In tetraethylammonium bromide–2,5-pyrrolidinedione (1/2) the bromide ion forms hydrogen bonds to the imide H atoms in the two succinimide molecules: $\text{Br}\cdots\text{N} = 3.338$ (11) and 3.380 (10) Å with $\text{N}\cdots\text{Br}\cdots\text{N} = 102.8$ (3)° and $\text{N—H}\cdots\text{Br} = 158$ and 178 °. The succinimide molecules are inclined at 63.72 (3)° to each other.

Comment

The title compound has been investigated as part of a study of N—Br—N bonding properties (Elding, Albertsson, Svensson & Ebersson, 1990; Elding, Larsson, Svensson, Albertsson & Ebersson, 1992). The solid complex was prepared by mixing *N*-bromosuccinimide (0.05 mole in 70 ml acetonitrile) with tetraethylammonium thiocyanate (0.05 mole in 15 ml acetonitrile) and then adding dry diethyl ether to the solution. The mixture was kept at 273 K for several days before the crystals were filtered off. This yielded a mixture of very small orange crystals, which could not be studied by single-crystal diffraction, and larger needle-shaped colourless crystals, of which one was chosen for this investigation.

The bromide ion is close to the NH groups in the two succinimide molecules (Fig. 1). The $\text{Br}\cdots\text{N}$ distances are 3.338 (11) and 3.380 (10) Å for N1 and N2, respectively. The H-atom positions were calculated with $\text{N—H} = 0.95$ Å. The resulting $\text{Br}\cdots\text{H}$ distances are 2.44 and 2.43 Å, more than 0.2 Å shorter than the sum of the van der Waals radii for Br and H (3.15 Å) (*Chemistry Data Book*, 1982). Thus, the bromide ion is hydrogen bonded to the succinimide molecules (Hamilton & Ibers, 1968). This is also indicated by the sum of the Br^- ionic radius (1.95 Å), the covalent radius of N (0.74 Å) and the covalent diameter of H (0.74 Å), which is 3.43 Å (*Chemistry Data Book*, 1982), *i.e.* close to the $\text{Br}\cdots\text{N}$ distances found. The shorter of the $\text{Br}\cdots\text{N}$ distances results in an angled hydrogen bond, $\text{N—H}\cdots\text{Br}$, and the longer in an almost linear one (Table 2). The angle $\text{N1}\cdots\text{Br}\cdots\text{N2} = 102.8$ (3)° is in good agreement

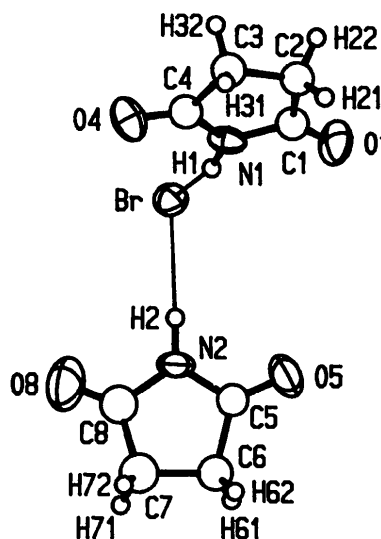


Fig. 1. Drawing of the bromide–succinimide (1/2) moiety in the structure. The H atoms are drawn with a small arbitrary radius. The displacement ellipsoids are scaled to include 50% probability.