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

C1—C2	1.514 (3)	C3—C4	1.519 (2)
C1—C6	1.511 (2)	C4—C5	1.523 (3)
C1—C1^{i}	1.339 (2)	C5—C6	1.529 (2)
C2—C3	1.531 (2)		
C2—C1—C6	111.04 (13)	C2—C3—C4	111.17 (14)
C1^{i}—C1—C2	124.55 (16)	C3—C4—C5	110.42 (13)
C1^{i}—C1—C6	124.40 (17)	C4—C5—C6	111.08 (14)
C1—C2—C3	111.88 (15)	C1—C6—C5	112.27 (14)

Symmetry code: (i) $2 - x, 1 - y, 1 - z$.

The adopted spacegroup, $P\bar{1}$, is consistent with the statistical $N(z)$ test for centrosymmetry and is confirmed by the successful refinement. Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989) with local modifications. Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1993). Program(s) used to solve structure: *SIR*92 (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *PLATON*93 (Spek, 1990). Software used to prepare material for publication: *PLATON*93.

This work was supported in part (ALS and NV) by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71795 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1118]

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343-350.
Barton, D. H. R. & Willis, B. J. (1972). *J. Chem. Soc. Perkin Trans.* 1, pp. 305-310.
Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* A**40**, C-410.
Buter, J., Wassenaar, S. & Kellogg, R. M. (1972). *J. Org. Chem.* **37**, 4045-4060.
Criegee, R., Vogel, E. & Horger, H. (1952). *Chem. Ber.* **85**, 144-152.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321-324.
Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. & Stewart, J. J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902-3909.
Enraf-Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
Friedli, A. C., Lynch, V. M., Kaszynski, P. & Michl, J. (1990). *Acta Cryst.* B**46**, 377-389.
Hehre, W. J., Radom, L., von Schleyer, R. P. & Pople, J. A. (1986). *Ab Initio Molecular Orbital Theory*. New York: John Wiley.
Hoogesteger, F. J., Havenith, R. W. A., Zwikker, J. W. & Jenneskens, L. W. (1994). In preparation.
Kaszynski, P., McMurdie, N. D. & Michl, J. (1991). *J. Org. Chem.* **56**, 307-316.
Kaszynski, P., Friedli, A. C. & Michl, J. (1992). *J. Am. Chem. Soc.* **114**, 601-620.
Murthy, G. S., Hassenrück, K., Lynch, V. M. & Michl, J. (1989). *J. Am. Chem. Soc.* **111**, 7262-7264.
Obeng, Y. S., Laing, M. E., Friedli, A. C., Yang, H. C., Wang, D., Thulstrup, E. W., Bard A. J. & Michl, J. (1992). *J. Am. Chem. Soc.* **114**, 9943-9952.
Sasvári, K. & Löw, M. (1965). *Acta Cryst.* **19**, 840-848.
Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination*. Univ. of Cambridge, England.
Spek, A. L. (1993). *HELENA. Program for Data Reduction*. Univ. of Utrecht, The Netherlands.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Zimmerman, H. E., King, R. K. & Meinhardt, M. B. (1992). *J. Org. Chem.* **57**, 5484-5492.

Acta Cryst. (1994). C**50**, 744-746

trans-transoid-trans-transoid-trans-Tetracyclo[$16.4.0.0^{2,9}.0^{10,17}$]docosa-5,13-diene

Anthony L. Spek

Bijvoet Center for Biomolecular Research,
Department of Crystal and Structural Chemistry,
Utrecht University, Padualaan 8, 3584 CH Utrecht,
The Netherlands

Petrus J. J. A. Timmermans and Adri Mackor

TNO Hoofdgroep Maatschappelijke Technologie,
PO Box 108, 3700 AC Zeist, The Netherlands

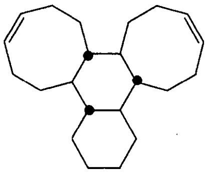
(*Received* 5 *August* 1993; *accepted* 29 *October* 1993)

Abstract

The title compound, $C_{22}H_{34}$, is obtained by cycloaddition of one cyclohexene and two 1,5-cyclooctadiene molecules, photoassisted by copper(I) trifluoromethanesulfonate. The crystal structure contains two crystallographically independent molecules, each positioned on sites with twofold axial symmetry. The two independent (half)-molecules show only minor differences.

Comment

The monoclinic unit cell contains four molecules of the title compound, (I) (Fig. 1), each located on a twofold axis. The geometries of the two crystallographically independent half-molecules are similar. The puckering of the central six-membered ring is best described as skew-boat (Boeyens, 1978) with puckering-analysis parameters (Cremer & Pople, 1975) $Q = 0.675$ (2) [0.676 (3)] Å, $\theta = 76.4$ (2) [75.6 (3)]°, $\varphi = 150.0$ (2) [150.0 (2)]° for molecule (1) [data for molecule (2) in square brackets]. The corresponding values of $Q = 0.546$ (3) [0.538 (3)] Å, $\theta = 9.5$ (3) [7.3 (3)]°, $\varphi = 150$ (2) [150 (3)]° for the other six-membered ring indicate a chair conformation.



(I)

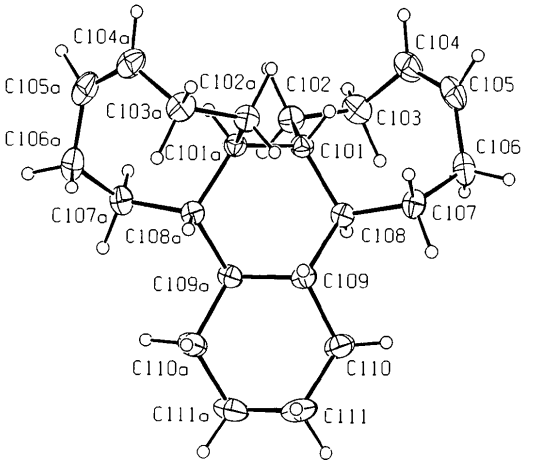


Fig. 1. Anisotropic displacement ellipsoid drawing (30% probability level) of one of the two crystallographically independent molecules, each sitting on a crystallographic twofold axis.

Experimental

Irradiation with 254 nm light of a dilute (1:10) solution (at 298 K) of 1,5-cyclooctadiene (COD) in cyclohexene, saturated with copper(I) trifluoromethanesulfonate, yielded a 1:2 C_6/C_8 cycloadduct as the major oligomeric product. The cyclohexene and two COD's are arranged around the central cyclohexane ring in an all-*trans* fashion.

Crystal data

$C_{22}H_{34}$
$M_r = 298.51$
Monoclinic
$P2/a$ (non-standard $P2/c$)
$(x, y, z; \frac{1}{2} - x, y, -z; -x, -y, -z; \frac{1}{2} + x, -y, z)$
$a = 14.742$ (2) Å
$b = 9.078$ (1) Å
$c = 15.162$ (2) Å
$\beta = 118.90$ (1)°
$V = 1776.4$ (4) Å^3

$Z = 4$
$D_x = 1.116$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 12\text{–}20°$
$\mu = 0.42$ mm^{-1}
$T = 294$ K
Plate
0.75 × 0.70 × 0.22 mm
Colorless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.76$, $T_{max} = 1.22$
14 373 measured reflections
3371 independent reflections

3260 observed reflections [$I > 2.5\sigma(I)$]
$R_{int} = 0.07$
$\theta_{max} = 70°$
$h = -17 \rightarrow 17$
$k = -11 \rightarrow 11$
$l = -18 \rightarrow 18$
2 standard reflections
frequency: 60 min
intensity variation: 3.5%

Refinement

Refinement on F
$R = 0.064$
$wR = 0.059$
$S = 0.79$

Unit weights applied
$(\Delta/\sigma)_{max} = 0.2$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

3260 reflections
335 parameters
All H-atom parameters refined

Atomic scattering factors from Cromer & Mann (1968)

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}
C101	0.19643 (16)	0.5566 (2)	0.45204 (16)	0.0351 (7)
C102	0.20371 (19)	0.4999 (3)	0.36026 (18)	0.0424 (8)
C103	0.0983 (2)	0.4775 (3)	0.26487 (18)	0.0489 (8)
C104	0.0262 (2)	0.3873 (3)	0.28594 (19)	0.0534 (9)
C105	−0.0376 (2)	0.4419 (4)	0.3164 (2)	0.0583 (10)
C106	−0.0536 (2)	0.6014 (3)	0.3298 (2)	0.0557 (9)
C107	0.02866 (19)	0.6765 (3)	0.42627 (19)	0.0468 (8)
C108	0.13323 (16)	0.7016 (2)	0.42915 (16)	0.0347 (7)
C109	0.19542 (17)	0.8329 (2)	0.49500 (17)	0.0375 (7)
C110	0.1372 (2)	0.9778 (3)	0.4507 (2)	0.0532 (9)
C111	0.2003 (2)	1.1146 (3)	0.5026 (2)	0.0632 (10)
C201	0.24273 (16)	0.9162 (2)	0.04688 (15)	0.0340 (6)
C202	0.34105 (19)	0.9715 (3)	0.14040 (18)	0.0420 (8)
C203	0.3285 (2)	0.9913 (3)	0.23497 (19)	0.0507 (9)
C204	0.2357 (2)	1.0832 (3)	0.21387 (19)	0.0546 (9)
C205	0.1408 (2)	1.0310 (3)	0.1809 (2)	0.0545 (9)
C206	0.1100 (2)	0.8703 (3)	0.1655 (2)	0.0545 (10)
C207	0.0987 (2)	0.7974 (3)	0.0691 (2)	0.0475 (8)
C208	0.20180 (17)	0.7712 (3)	0.06894 (16)	0.0366 (7)
C209	0.19944 (18)	0.6404 (3)	0.00364 (17)	0.0388 (7)
C210	0.1852 (3)	0.4953 (3)	0.0479 (2)	0.0546 (10)
C211	0.1980 (3)	0.3576 (3)	−0.0023 (2)	0.0646 (10)

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

C101—C102	1.535 (3)	C201—C202	1.542 (3)
C101—C108	1.552 (3)	C201—C208	1.550 (3)
C101—C101^i	1.546 (3)	C201—C201^{ii}	1.537 (3)
C102—C103	1.541 (4)	C202—C203	1.542 (4)
C103—C104	1.493 (4)	C203—C204	1.499 (4)
C104—C105	1.328 (5)	C204—C205	1.325 (4)
C105—C106	1.497 (5)	C205—C206	1.512 (4)
C106—C107	1.536 (4)	C206—C207	1.538 (4)
C107—C108	1.538 (4)	C207—C208	1.540 (4)
C108—C109	1.541 (3)	C208—C209	1.536 (4)
C109—C110	1.537 (3)	C209—C210	1.538 (4)
C109—C109^i	1.542 (4)	C209—C209^{ii}	1.547 (4)
C110—C111	1.523 (4)	C210—C211	1.522 (4)
C111—C111^i	1.504 (5)	C211—C211^{ii}	1.501 (7)
C102—C101—C108	112.27 (18)	C202—C201—C208	111.65 (18)
C101^i—C101—C102	111.4 (2)	C201^{ii}—C201—C202	111.2 (2)
C101^i—C101—C108	116.13 (16)	C201^{ii}—C201—C208	116.26 (16)
C101—C102—C103	114.5 (2)	C201—C202—C203	114.3 (2)
C102—C103—C104	111.8 (2)	C202—C203—C204	111.9 (2)
C103—C104—C105	124.5 (3)	C203—C204—C205	124.7 (3)
C104—C105—C106	126.4 (3)	C204—C205—C206	125.9 (3)
C105—C106—C107	117.1 (2)	C205—C206—C207	116.6 (2)
C106—C107—C108	114.3 (2)	C206—C207—C208	114.5 (2)
C101—C108—C107	111.46 (18)	C201—C208—C207	110.9 (2)
C101—C108—C109	113.98 (19)	C201—C208—C209	114.0 (2)
C107—C108—C109	114.0 (2)	C207—C208—C209	113.9 (2)
C108—C109—C110	110.3 (2)	C208—C209—C210	110.3 (2)
C108—C109—C109^i	109.25 (19)	C208—C209—C209^{ii}	108.9 (2)
C109^i—C109—C110	112.3 (2)	C209^{ii}—C209—C210	111.7 (3)
C109—C110—C111	113.6 (2)	C209—C210—C211	114.2 (3)
C110—C111—C111^i	109.9 (2)	C210—C211—C211^{ii}	110.3 (3)

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

X-ray data were collected for a transparent crystal glued on top of a glass fibre. The lattice was tested for higher metrical symmetry (Spek, 1988). The observed non-primitive pseudo-orthorhombic symmetry of the lattice is not supported by the corresponding Laue symmetry. Data collection: *CAD-4 Soft-*

ware (Enraf-Nonius, 1989) with local modifications. Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1990*a*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *PLATON*93 (Spek, 1990*b*). Software used to prepare material for publication: *PLATON*93.

X-ray data were collected by A. J. M. Duisenberg. This work was supported in part (ALS, PJJAT) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1112). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* **A40**, C-410.

Boeyens, J. C. A. (1978). *J. Cryst. Mol. Struct.* **8**, 317-320.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354-1358.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321-324.

Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Program for Crystal Structure Solution.* Univ. of Göttingen, Germany.

Spek, A. L. (1988). *J. Appl. Cryst.* **21**, 578-579.

Spek, A. L. (1990*a*). *HELENA. Program for Data Reduction.* Univ. of Utrecht, The Netherlands.

Spek, A. L. (1990*b*). *Acta Cryst.* **A46**, C-34.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158-166.

Acta Cryst. (1994). **C50**, 746–749

1-Deoxynojirimycin Hydrochloride

ANTHONY LINDEN

Organisch-chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

ROLAND HOOS AND ANDREA VASELLA

Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich, Switzerland

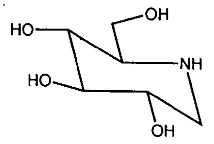
(*Received* 18 *October* 1993; *accepted* 4 *November* 1993)

Abstract

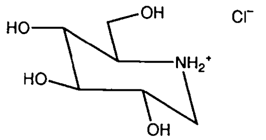
The structure of the hydrochloride salt of 1-deoxynojirimycin [(1*R*,3*R*,4*R*,5*S*)-3,4,5-trihydroxy-2-(hydroxymethyl)piperidinium chloride, $C_6H_{14}NO_4^+.Cl^-$] is reported. The cation has an almost undistorted $^4C_1$ conformation. The crystal structure is built up from alternating layers of cations and anions interconnected by a three-dimensional network of hydrogen bonds. Each chloride ion is coordinated through four hydrogen bonds and there are also two intercationic hydrogen bonds.

Comment

1-Deoxynojirimycin [1,5-dideoxy-1,5-imino-glucitol (I)] is a strong competitive inhibitor of α- and β-glucosidases (Legler, 1990). It has been isolated from various strains of *Bacillus* (Schmidt, Frommer, Müller & Truscheit, 1979), from plants of the genus *Morus* (Yagi, Kouno, Aoyagi & Murai, 1976) and from the root bark of the mulberry tree (Daigo, Inamori & Takemoto, 1986). It has been synthesized by a variety of routes (*e.g.* Paulsen, Sangster & Heyns, 1967; Inouye, Tsuruoka, Ito & Niida, 1968; Vasella & Voeffray, 1982; Bernotas & Ganem, 1985; Beaupere, Stasik, Uzan & Demailly, 1989; Fleet, Carpenter, Petursson & Ramsden, 1990; Ermert & Vasella, 1991). As a result of its inhibitory potential and its stability in water, it has been used in glycobiology (Winchester & Fleet, 1992) for such purposes as altering the processing of N-linked glycoproteins (Elbein, 1987) or inhibition of syncytium formation of HIV-infected cells (Gruters *et al.*, 1987). The mechanism of inhibition exerted by (I) is still unclear. It is neither a transition-state analogue (Dale, Ensley, Kern, Sastry & Byers, 1985) nor, presumably, a substrate analogue. The X-ray structure of the complex between (I) and the glucoamylase from *Aspergillus awamori* var. X100 has been published recently (Harris, Aleshin, Firsow & Honzatko, 1993). The resolution of the study (2.4 Å) did not permit the determination of the conformation of the inhibitor at the active site. According to NMR studies (Ermert & Vasella, 1991) the conformation of (I) and the hydrochloride (II) in aqueous solution is $^4C_1$. The X-ray structure determination of the hydrochloride (II), reported here, complements the existing structural information.



(I)



(II)

A view of the cation showing the atom-numbering scheme is shown in Fig. 1. The absolute configuration of (II) was assigned to agree with that of its known precursor, D-glucose, and was further confirmed by the X-ray analysis.

The bond lengths and angles within the cation exhibit normal values, although the C(1)—N(5)—C(5) angle has opened to 113.5 (1)°. The ring conformation is $^4C_1$ and the torsion angles around the piperidine ring show that the