VMS 5.2. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*93.

Financial support from the Ministry for Science and Technology, Republic of Slovenia, is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1075). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Golič, L. & Leban, I. (1978*a*). *Cryst. Struct. Commun.* **7**, 47–52.
Golič, L. & Leban, I. (1978*b*). *Cryst. Struct. Commun.* **7**, 53–57.
Golič, L. & Leban, I. (1980*a*). *Acta Cryst.* **B36**, 1520–1522.
Golič, L. & Leban, I. (1980*b*). *Cryst. Struct. Commun.* **9**, 739–744.
Golič, L. & Leban, I. (1981). *Cryst. Struct. Commun.* **10**, 221–226.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Mallinson, P. R. & Muir, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement*. Univ. of Göttingen, Germany.
Zupančič, N. & Šket, B. (1992). *J. Chem. Soc. Perkin Trans.* 1, pp. 179–180.

Acta Cryst. (1994). **C50**, 1467–1469

A Novel Dioxabicyclo[3.3.1]nonane, a Key Intermediate in the Synthesis of Erythronolide B *seco*-Acid

Vincent M. Lynch, Wen-Cherng Lee, Stephen F. Martin and Brian E. Davis

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712, USA

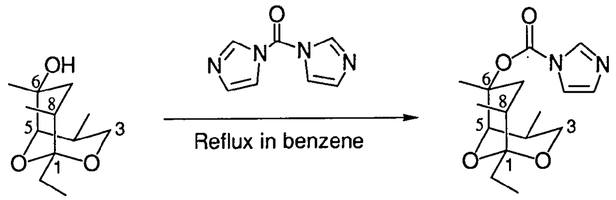
(*Received* 17 *September* 1992; *accepted* 18 *November* 1993)

Abstract

In the title compound, (1*R*,4*S*,5*R*,6*R*,8*R*)-1-ethyl-4,6,8-trimethyl-2,9-dioxabicyclo[3.3.1]nonan-6-yl 1-imidazolecarboxylate, $C_{16}H_{24}N_2O_4$, the 2,9-dioxabicyclo[3.3.1]nonane ring system assumes a double-chair conformation. Bond angles around the ring are enlarged compared to normal tetrahedral values to alleviate some of the overcrowding which results from close intramolecular H···H and C···C contacts. The *N*-imidazolylcarbonyloxy group is nearly planar with dihedral angles of 5.2 (2) and 6.0 (2)° between the imidazole and carbonyl groups for molecules 1 and 2, respectively.

Comment

The title compound, (II), was synthesized by refluxing 1-ethyl-4,6,8-trimethyl-2,9-dioxabicyclo[3.3.1]nonan-6-ol, (I), with 1,1′-carbonyldiimidazole in benzene (Martin, Pacofsky, Gist & Lee, 1989). The crystal structure determination of (II) was undertaken as part of a project aimed at the total syntheses of erythromycins A and B utilizing novel synthetic strategies (Martin *et al.*, 1989).



(I) (II)

There are two independent molecules in the asymmetric unit. They will be referred to as molecule 1 and molecule 2. Atoms of molecule 2 have labels appended with a prime. There are no significant differences in geometry or conformation between the two molecules. The dioxabicyclo[3.3.1]nonane ring system is found to have a double-chair conformation. This conformation results in the close proximity of the H atoms in the 3*a* and 7*a* positions. Constraining the bond lengths and angles to idealized values for bicyclo[3.3.1]nonane would result in the distance between these H atoms being 0.76 Å (Peters, Baas, van de Graaf, van der Toorn & van Bekkum, 1978). In the present case, the distances are 1.96 (5) and 1.98 (4) Å for molecules 1 and 2, respectively. The molecule adjusts to minimize these close contacts by expanding the appropriate angles at atoms around the ring system. In the present example, angles C4—C5—C6 and C1—O2—C3 are enlarged significantly. The angle at C4—C5—C6 is 121.9 (3) and 122.3 (3)° for molecules 1 and 2, respectively, while C1—O2—C3 is 116.8 (2) and 117.6 (3)°, respectively. Although the double-chair is the usual conformation for such a molecule lacking bulky groups at the 3*a* and/or the 7*a* positions (Peters *et al.*, 1978), the presence of axial Me groups at C6 and C8 was expected to force the ring into a chair–boat conformation. The C13···C14 contacts are the same for both molecules [3.356 (6) Å for molecule 1, 3.355 (5) Å for molecule 2]. Even though this diaxial interaction is energetically costly (Allinger & Miller, 1961), the *N*-imidazolylcarbonyloxy group at C6 would apparently encounter highly unfavorable steric interactions in the alternative chair–boat or boat–boat conformations.

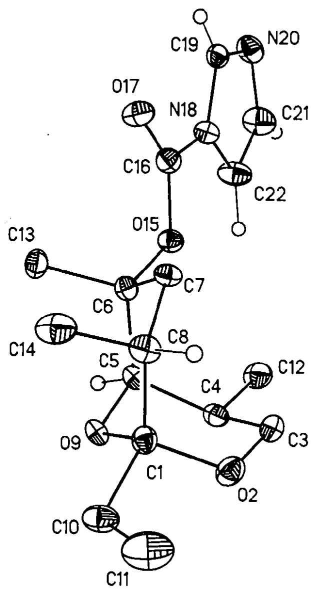


Fig. 1. View of molecule 1 of (1) showing the atom-labeling scheme and illustrating the double-chair conformation of the dioxabicyclo[3.3.1]nonane ring system. Displacement ellipsoids are scaled to the 30% probability level. Most H atoms have ben omitted for clarity.

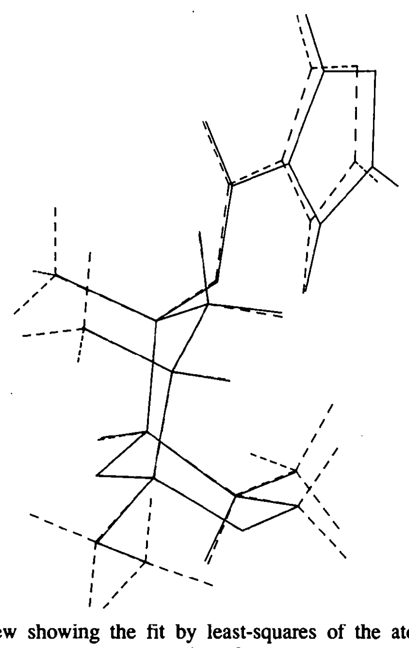


Fig. 2. View showing the fit by least-squares of the atoms of the dioxabicyclo[3.3.1]nonane portion of molecule 1 (dashed lines) onto those of molecule 2 (solid lines).

Experimental

Crystal data

$C_{16}H_{24}N_2O_4$	Mo $K\alpha$ radiation
$M_r = 308.38$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 40 reflections
$P2_1$	$\theta = 9.2–12.1°$
$a = 9.2100$ (11) Å	$\mu = 0.086$ mm^{-1}
$b = 10.156$ (2) Å	$T = 173$ (1) K
$c = 17.575$ (2) Å	Plate
$\beta = 103.631$ (10)°	0.73 × 0.36 × 0.16 mm
$V = 1597.5$ (4) Å^3	Colorless
$Z = 4$	
$D_x = 1.28$ Mg m^{-3}	

Data collection

Nicolet *R*3 diffractometer	$\theta_{max} = 25.0°$
ω scans	$h = -10 \rightarrow 10$
Absorption correction: none	$k = 0 \rightarrow 12$
6258 measured reflections	$l = -20 \rightarrow 20$
2999 independent reflections	4 standard reflections monitored every 96 reflections
2471 observed reflections [$F > 4.0\sigma(F)$]	intensity variation: 1.56%
$R_{int} = 0.0177$	

Refinement

Refinement on F	$\Delta\rho_{max} = 0.18$ e Å^{-3}
$R = 0.0336$	$\Delta\rho_{min} = -0.16$ e Å^{-3}
$wR = 0.0336$	Extinction correction: modified Larson (1982); *SHELXTL-Plus* (Sheldrick, 1991)
$S = 1.07$	Extinction coefficient: 1.4 (2) × 10^{-6}
2471 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
589 parameters	
All H-atom parameters refined	
Calculated weights $w = 1/[\sigma^2(F) + 0.0004F^2]$	
$(\Delta/\sigma)_{max} = 0.0742$	

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

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

	x	y	z	U_{eq}
C1	0.7191 (4)	0.7150 (4)	0.4201 (2)	0.0286 (12)
O2	0.8434 (3)	0.76451†	0.47810 (13)	0.0353 (8)
C3	0.8936 (4)	0.6862 (5)	0.5471 (2)	0.0340 (12)
C4	0.7661 (4)	0.6354 (4)	0.5783 (2)	0.0277 (12)
C5	0.6439 (3)	0.5754 (4)	0.5133 (2)	0.0241 (11)
C6	0.6706 (3)	0.4493 (4)	0.4694 (2)	0.0242 (10)
C7	0.7869 (4)	0.4704 (4)	0.4221 (2)	0.0272 (12)
C8	0.7640 (4)	0.6002 (4)	0.3739 (2)	0.0310 (12)
O9	0.5997 (2)	0.6752 (3)	0.45443 (11)	0.0247 (7)
C10	0.6588 (5)	0.8361 (5)	0.3714 (2)	0.0364 (14)
C11	0.7696 (7)	0.9035 (6)	0.3334 (3)	0.062 (2)
C12	0.8196 (5)	0.5528 (5)	0.6526 (2)	0.041 (2)
C13	0.5205 (4)	0.4008 (5)	0.4219 (2)	0.0324 (12)
C14	0.6551 (6)	0.5811 (5)	0.2940 (2)	0.045 (2)
O15	0.7285 (2)	0.3529 (3)	0.53320 (12)	0.0263 (7)
C16	0.7482 (3)	0.2287 (4)	0.5146 (2)	0.0287 (12)
O17	0.7339 (3)	0.1816 (4)	0.45080 (14)	0.0370 (9)
N18	0.7935 (3)	0.1517 (4)	0.5829 (2)	0.0287 (10)
C19	0.8311 (4)	0.0217 (4)	0.5831 (2)	0.0297 (11)
N20	0.8663 (3)	−0.0273 (4)	0.6535 (2)	0.0407 (11)

C21	0.8476 (5)	0.0758 (5)	0.7014 (3)	0.047 (2)
C22	0.8044 (5)	0.1863 (5)	0.6605 (2)	0.042 (2)
C1′	0.2075 (3)	0.6367 (4)	−0.0719 (2)	0.0230 (10)
O2′	0.1363 (2)	0.5924 (3)	−0.01205 (12)	0.0294 (8)
C3′	0.1513 (4)	0.6732 (4)	0.0564 (2)	0.0283 (11)
C4′	0.3103 (4)	0.7209 (4)	0.0857 (2)	0.0264 (11)
C5′	0.3710 (4)	0.7779 (4)	0.0183 (2)	0.0227 (11)
C6′	0.3059 (3)	0.9036 (4)	−0.0262 (2)	0.0224 (10)
C7′	0.1451 (3)	0.8830 (4)	−0.0727 (2)	0.0272 (11)
C8′	0.1208 (4)	0.7519 (4)	−0.1191 (2)	0.0263 (11)
O9′	0.3583 (2)	0.6753 (3)	−0.03946 (11)	0.0231 (7)
C10′	0.2184 (4)	0.5129 (4)	−0.1186 (2)	0.0307 (12)
C11′	0.0688 (5)	0.4474 (5)	−0.1533 (2)	0.0385 (14)
C12′	0.3288 (5)	0.8052 (5)	0.1590 (2)	0.0340 (15)
C13′	0.4122 (4)	0.9489 (4)	−0.0751 (2)	0.0277 (11)
C14′	0.1572 (4)	0.7683 (5)	−0.1997 (2)	0.0341 (14)
O15′	0.3082 (2)	1.0011 (3)	0.03736 (12)	0.0261 (7)
C16′	0.2716 (3)	1.1252 (4)	0.0182 (2)	0.0283 (11)
O17′	0.2284 (3)	1.1721 (4)	−0.04566 (13)	0.0370 (9)
N18′	0.2864 (3)	1.2022 (4)	0.0864 (2)	0.0274 (10)
C19′	0.2422 (4)	1.3323 (4)	0.0855 (2)	0.0308 (12)
N20′	0.2641 (3)	1.3804 (4)	0.1556 (2)	0.0437 (12)
C21′	0.3272 (5)	1.2782 (5)	0.2044 (3)	0.052 (2)
C22′	0.3419 (5)	1.1697 (5)	0.1640 (2)	0.045 (2)

† Coordinate fixed to define origin.

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

	(I)	(II)
O2—C1	1.433 (4)	1.437 (4)
C8—C1	1.532 (6)	1.543 (5)
O9—C1	1.431 (4)	1.427 (4)
C10—C1	1.527 (6)	1.517 (6)
C3—O2	1.433 (4)	1.435 (5)
C4—C3	1.500 (6)	1.513 (5)
C5—C4	1.529 (4)	1.536 (5)
C12—C4	1.532 (5)	1.523 (5)
C6—C5	1.544 (6)	1.543 (5)
O9—C5	1.436 (4)	1.440 (4)
C7—C6	1.519 (5)	1.529 (4)
C13—C6	1.518 (5)	1.518 (5)
O15—C6	1.490 (4)	1.489 (5)
C8—C7	1.554 (6)	1.549 (5)
C14—C8	1.534 (5)	1.539 (5)
C11—C10	1.509 (8)	1.522 (5)
C16—O15	1.327 (5)	1.327 (5)
O17—C16	1.197 (5)	1.197 (4)
N18—C16	1.411 (5)	1.411 (5)
C19—N18	1.365 (6)	1.381 (6)
C22—N18	1.389 (5)	1.378 (5)
N20—C19	1.302 (5)	1.296 (5)
C21—N20	1.380 (6)	1.385 (6)
C22—C21	1.342 (7)	1.335 (7)
O2—C1—C8	112.0 (3)	111.3 (3)
O2—C1—O9	111.3 (2)	111.2 (2)
C8—C1—O9	109.8 (3)	109.8 (3)
C8—C1—C10	115.0 (3)	115.5 (3)
O9—C1—C10	104.5 (3)	105.2 (3)
C10—C1—O2	103.9 (3)	103.7 (3)
C3—O2—C1	116.8 (2)	117.6 (3)
C4—C3—O2	112.1 (3)	111.3 (3)
C5—C4—C12	116.8 (4)	116.9 (3)
C5—C4—C3	111.4 (3)	110.9 (2)
C12—C4—C3	112.2 (3)	112.0 (3)
C6—C5—O9	106.1 (3)	106.5 (2)
C6—C5—C4	121.9 (3)	122.3 (3)
O9—C5—C4	106.9 (3)	106.7 (3)
C7—C6—C13	114.4 (3)	114.3 (3)
C7—C6—O15	109.4 (3)	109.5 (3)
C7—C6—C5	111.9 (3)	111.7 (3)
C13—C6—O15	108.5 (3)	109.0 (3)
C13—C6—C5	108.2 (3)	108.2 (3)
O15—C6—C5	103.9 (2)	103.6 (2)
C8—C7—C6	113.3 (3)	113.6 (3)
C14—C8—C1	112.5 (3)	112.3 (3)
C14—C8—C7	111.5 (3)	110.8 (3)
C1—C8—C7	112.0 (3)	112.1 (3)
C1—O9—C5	112.7 (2)	113.0 (3)
C11—C10—C1	114.8 (4)	114.2 (3)
C16—O15—C6	119.0 (3)	118.9 (3)
O17—C16—N18	121.4 (4)	121.3 (4)
O17—C16—O15	128.2 (4)	128.6 (4)
N18—C16—O15	110.3 (3)	110.0 (3)
C19—N18—C22	106.5 (3)	106.3 (3)
C19—N18—C16	124.2 (3)	123.4 (3)
C22—N18—C16	129.3 (4)	130.3 (4)
N20—C19—N18	112.2 (3)	111.7 (3)
C21—N20—C19	104.5 (4)	104.8 (4)
C22—C21—N20	111.8 (4)	111.6 (4)
N18—C22—C21	104.9 (4)	105.6 (4)

The *y*-coordinate of O2 was fixed to define the origin along the *b* axis. The absolute configuration was assigned by internal comparison (Lynch, Lee, Martin & Davis, 1991, 1992; Lynch, Pacofsky, Martin & Davis, 1989; Lynch, Mulhern & Martin, 1987). Structure refinement and manuscript preparation were performed on a VAXstation II. Data collection and cell refinement: Siemens *P3/V* data collection system. Data reduction, structure solution and refinement, and molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *FUER* (Larson, 1982); *MPLN* (Cordes, 1983).

The authors wish to thank the Robert A. Welch Foundation (F-652) and the National Institutes of Health (GM 31077) for their support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HH1043). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allinger, N. L. & Miller, M. L. (1961). *J. Am. Chem. Soc.* **83**, 2145–2150.

Cordes, A. W. (1982). *MPLN. Program to Calculate Least-Squares Planes and Dihedral Angles with Associated e.s.d.'s.* Univ. of Arkansas, Fayetteville, USA.

Larson, S. B. (1982). *FUER. Program for Generating Positional and Thermal Parameters and Geometrical Quantities.* Univ. of Texas, Austin, USA.

Lynch, V. M., Lee, W.-C., Martin, S. F. & Davis, B. E. (1991). *Acta Cryst.* C**47**, 1117–1120.

Lynch, V. M., Lee, W.-C., Martin, S. F. & Davis, B. E. (1992). *Acta Cryst.* C**48**, 1145–1148.

Lynch, V. M., Mulhern, T. A. & Martin, S. F. (1987). *Acta Cryst.* C**43**, 2237–2238.

Lynch, V. M., Pacofsky, G. J., Martin, S. F. & Davis, B. E. (1989). *Acta Cryst.* C**45**, 973–975.

Martin, S. F., Pacofsky, G. J., Gist, R. P. & Lee, W.-C. (1989). *J. Am. Chem. Soc.* **111**, 7634–7636.

Peters, J. A., Baas, J. M. A., van de Graaf, B., van der Toorn, J. M. & van Bekkum, H. (1978). *Tetrahedron*, **34**, 3313–3323.

Sheldrick, G. M. (1991). *SHELXTL-Plus.* Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.