Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2326 measured reflections
2214 independent reflections
1774 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\rm max} = 29.96°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.057$
$S = 0.875$
2214 reflections
281 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0202P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.175$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.105$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.007 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.06 (6)

Table 1. *Selected torsion angles (°)*

C6—O1—C1—C10b	51.9 (2)	C2—C1—C10b—C4a	−57.2 (2)
C10b—C1—C2—C3	34.2 (3)	C10—C10a—C10b—C1	141.6 (2)
C11—C4—C4a—N	24.2 (2)	C6a—C10a—C10b—C1	36.3 (2)
C1—O1—C6—O2	167.5 (2)	C4a—C4—C11—C12	−3.1 (3)
C1—O1—C6—C6a	−13.6 (3)	C4—C11—C12—N	−19.3 (3)
O1—C1—C10b—C4a	62.0 (2)		

The positions of 13 H atoms were computed. 11 H atoms were located from a difference map and the remaining two (on water molecules) were not located. The computed H atoms were refined isotropically using a riding model and an overall $U_{\rm iso}$, while the remaining H atoms were refined freely.

Data collection: *CAD-4/PC* (Kretschmar, 1996). Cell refinement: *CAD-4/PC*. Data reduction: *CFEO* (Solans, 1978). Program(s) used to solve structure: *SHELXS*-97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP* (Brueggemann & Schmid, 1990). Software used to prepare material for publication: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1288). Services for accessing these data are described at the back of the journal.

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(3*R*)-4,4-Dimethyl-2-oxotetrahydrofuran-3-yl (2*S*)-7-methoxy-2,3-dihydro-1,4-benzodioxin-2-carboxylate

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Abstract

The structure of the title compound, $C_{16}H_{18}O_7$, a key intermediate in the synthesis of antagonist adrenergic agents, is reported. The 1,4-benzodioxin ring shows a half-chair form with a Csp^3 atom out of the plane

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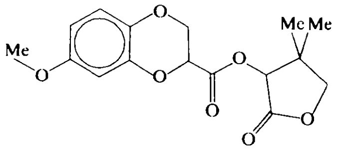
defined by the remaining atoms. The lactone ring shows an envelope form.

Comment

The 2,3-dihydro-1,4-benzodioxin ring system has been widely used in medicinal chemistry, particularly in the design of cardiovascular agents such as α- and β-adrenergic antagonists (Timmermans & Van Zwieten, 1982; Giardinà *et al.*, 1985; Khouili *et al.*, 1996*a*). It has been shown that the absolute stereochemistry at the stereogenic centre in 2-substituted 2,3-dihydro-1,4-benzodioxin derivatives is of prime importance for both affinity and selectivity (Khouili *et al.*, 1996*b*).

The lactone ring in the title compound, (I), has an envelope form with the C13 atom −0.564 (2) Å out of the plane defined by the remaining four atoms. A study of the Cambridge Structural Database (Allen & Kennard, 1993) indicates that for 33 out of 57 observations the lactone moiety adopts this form, and for 18 other observations a skew-envelope form. Among the compounds having an envelope form the title compound shows the largest deviation of an atom out of the lactone plane.



(I)

The C1, C9, O3, O4 and C10 atoms are in a plane. The dihedral angles with the lactone ring and the 1,4-benzodioxin moiety are 152.30 (19) and 88.8 (2)°, respectively. The 1,4-benzodioxin moiety shows an envelope form with the C8 atom −0.631 (2) Å out of the plane defined by the remaining nine atoms. Usually, the 1,4-benzodioxin moiety shows a twist-planar form with atoms in positions 2 and 3 out of the plane (25 of 29 observations in the Cambridge Structural Database). The envelope form (four of 29 observations) is observed when the C atom of the substituent linked to position 2 has an electronic delocalization and when position 3 bears two H atoms.

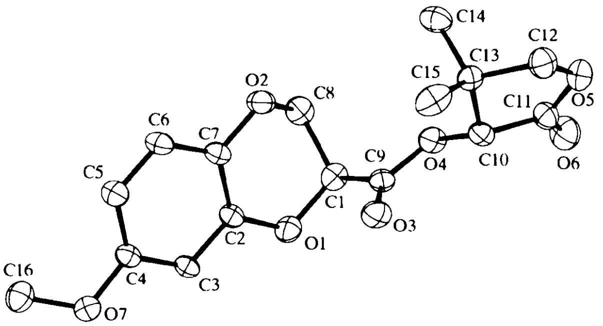


Fig. 1. Molecular structure showing 50% probability displacement ellipsoids.

Experimental

The reaction of 7-methoxy-2-carboxy-2,3-dihydro-1,4-benzodioxin with the chiral alcohol (*R*)-(−)-pantolactone gave a mixture of the two diastereomeric esters. A lactone ring was used as an auxiliary chiral centre, because it is easily hydrolysed. The esters were separated by flash chromatography (Et_2O:CH_2Cl_2, 2:98) and the diastereoisomeric purity was assayed by HPLC (enantiomeric excess > 99%) (Khouili *et al.*, 1994). Crystals of title compound were obtained by diffusion of hexane from an ethyl acetate solution.

Crystal data

$C_{16}H_{18}O_7$
$M_r = 322.30$
Orthorhombic
$P2_12_12_1$
$a = 10.313(4)$ Å
$b = 11.871(2)$ Å
$c = 12.713(2)$ Å
$V = 1556.4(7)$ Å^3
$Z = 4$
$D_x = 1.375$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12$–$21°$
$\mu = 0.109$ mm^{-1}
$T = 298(2)$ K
Prism
0.4 × 0.2 × 0.2 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2587 measured reflections
2555 independent reflections
2234 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.010$
$\theta_{\max} = 29.93°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.152$
$S = 1.049$
2555 reflections
266 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.1183P)^2 + 0.0310P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.007$

$\Delta\rho_{\max} = 0.311$ e Å^{-3}
$\Delta\rho_{\min} = -0.250$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.098 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C2	1.374 (3)	O5—C11	1.325 (3)
O1—C1	1.421 (3)	O5—C12	1.465 (4)
O2—C7	1.385 (3)	C1—C9	1.514 (3)
O2—C8	1.426 (3)		
O1—C2—C7	122.4 (2)	O3—C9—O4	125.0 (2)
O7—C4—C3	115.7 (2)	O3—C9—C1	125.9 (2)
O7—C4—C5	124.6 (2)	O4—C9—C1	109.1 (2)
O2—C7—C2	121.0 (2)		
C2—O1—C1—C9	88.8 (2)	C10—O4—C9—O3	−2.7 (3)
C1—O1—C2—C7	5.1 (3)	O1—C1—C9—O3	−12.3 (3)
C8—O2—C7—C2	26.4 (3)	C9—O4—C10—C11	152.3 (2)

The positions of five H atoms were computed; the remaining H atoms were located from a difference map. The computed H atoms were refined isotropically using a riding model, while the remaining H atoms were refined independently.

Data collection: *CAD-4/PC* (Kretschmar, 1996). Cell refinement: *CAD-4/PC*. Data reduction: *CFEO* (Solans, 1978). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*). Molecular graphics: *ORTEP* (Brueggemann & Schmid, 1990). Software used to prepare material for publication: *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1024). Services for accessing these data are described at the back of the journal.

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5′-*O*-(Toluenesulfonyl)adenosine

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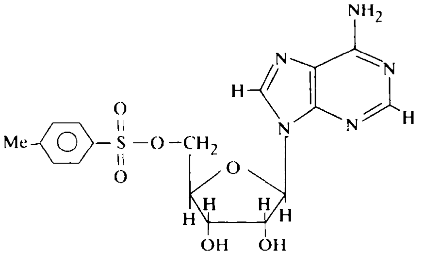
Abstract

The title compound, $C_{17}H_{19}N_5O_6S$, crystallizes from a water–acetone solution. The adenine base is in an *anti* conformation, with a glycosyl torsion angle of −166.5 (4)°. The ribose sugar adopts an envelope conformation (^3E). The toluenesulfonyl moiety is nearly perpendicular to the base. Both Watson–Crick and Hoogsteen sites, N1 and N6, and N6 and N7, of the adenine base are involved in a pair of hydrogen bonds, forming an *A.A.A* triplet pattern in the crystal lattice.

Comment

As part of our systematic X-ray studies on ribose/deoxyribose nucleosides and nucleotides (Padiyar & Seshadri, 1996; Mande *et al.*, 1994; Krishnan & Seshadri, 1992), we report here the crystal structure of 5′-*O*-(toluenesulfonyl)adenosine, (I). We were also interested in studying the effect of the bulky substituent on the conformation of the nucleoside molecule.



(I)

The glycosyl torsion angle [C4—N9—C1′—O4′] of −166.5 (4)° indicates an *anti* conformation. The ribofuranose ring is C3′-*endo* puckered. The pseudorotation parameters (Altona & Sundaralingam, 1972) are P = 19.1° and τ_m = 35.5°. The exocyclic torsion angle about the C4′—C5′ bond is g^+. The toluenesulfonyl moiety is nearly perpendicular to the adenine base.

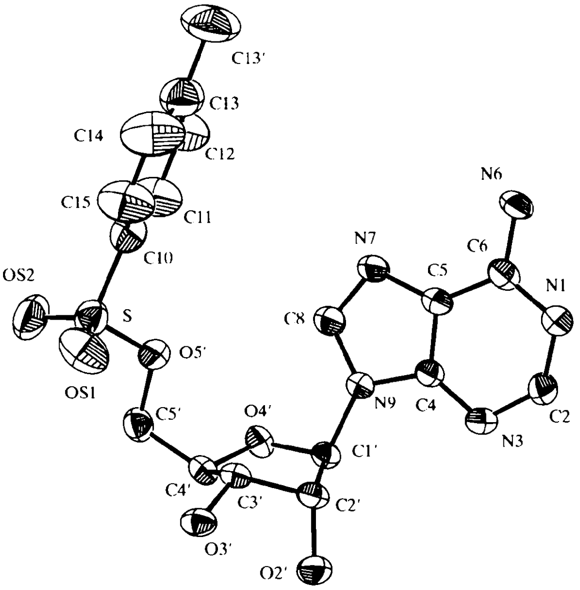


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.