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Three 1,3,4-Trisubstituted β-Lactam Antibiotics

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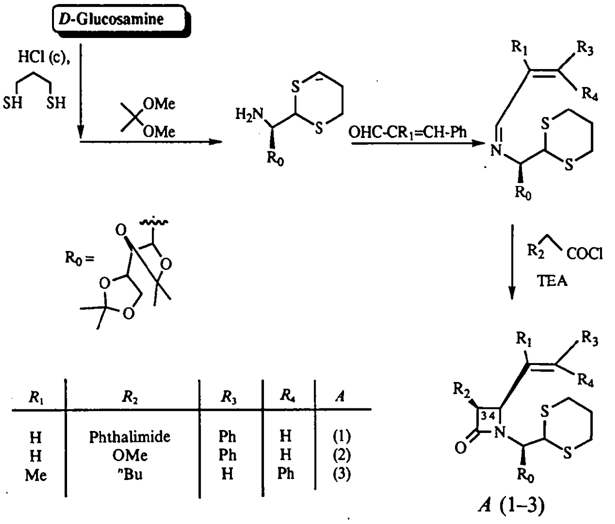
(*Received* 5 *January* 1994; *accepted* 4 *February* 1994)

Abstract

Monobactams (2-azetidinones) are four-membered cyclic amides which exhibit very important antibacterial properties, as well as β-lactamase- and elastase-inhibitory activities. A stereoselective asymmetric synthesis of 1,3,4-trisubstituted and 3,4-disubstituted 2-azetidinones was performed using D-glucosamine as the chiral auxiliary *via* a Staudinger [2+2] cycloaddition. The absolute stereochemistries at C3 and C4 of three of these potential therapeutic substances: 2-[1-{(1,3-dithian-2-yl)[2,2,2′,2′-tetramethyl-4,4′-bi(1,3-dioxolanyl)-5-yl]methyl}-2-oxo-4-(*E*)-styrylazetidin-3-yl]isoindol-1,3-dione, (1), 1-{(1,3-dithian-2-yl)[2,2,2′,2′-tetramethyl-4,4′-bi(1,3-dioxolanyl)-5-yl]methyl}-3-methoxy-4-(*E*)-styrylazetidin-2-one, (2), and 3-butyl-1-{(1,3-dithian-2-yl)[2,2,2′,2′-tetramethyl-4,4′-bi(1,3-dioxolanyl)-5-yl]methyl}-4-[1-methyl-(*Z*)-styryl]azetidin-2-one, (3), have been established by X-ray diffraction analyses. The four-membered ring is quite planar in compounds (1) and (3), but slightly bent in (2). The arrangement of the substituents in the vicinity of the lactam ring is similar in (1) and (3), but in (2) the dithiane ring is rotated around the N1—C2′ bond by approximately 120°.

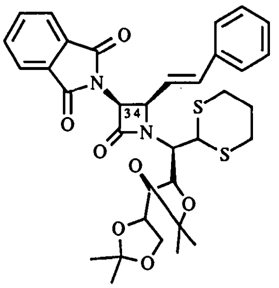
Comment

Monobactams (2-azetidinones) are four-membered cyclic amides. They exhibit very important antibacterial properties, as well as β-lactamase- and elastase-inhibitory activities (Mascaretti, Roveri & Danelon, 1993; Firestone, Barker, Pisano, Ashe & Dahlgren, 1990; Maillard *et al.*, 1990; Hagmann *et al.*, 1991, 1992). They have also been reported as potential hypocholesterolemic agents (Burnett *et al.*, 1991) and trombin inhibitors (Han, 1990). Recently, we published (Barton *et al.*, 1990; Adonias *et al.*, 1993) an asymmetric synthesis of 1,3,4-trisubstituted and 3,4-disubstituted 2-azetidinones, using D-glucosamine as chiral auxiliary, *via* a Staudinger [2+2] cycloaddition. The compounds (1), (2) and (3) were prepared in good overall yields according to the scheme below. Complete diastereospecificity was observed for compounds (1) and (3), while a 2:1 mixture of two *cis*-monobactams was obtained in the synthesis of (2). The *cis* orientation of the substituents

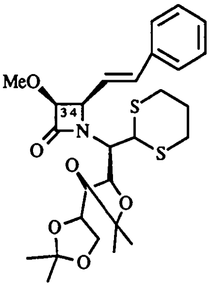


R_1	R_2	R_3	R_4	A
H	Phthalimide	Ph	H	(1)
H	OMe	Ph	H	(2)
Me	^{n}Bu	H	Ph	(3)

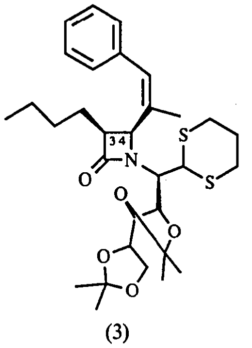
A (1–3)



(1)



(2)



(3)

at C3 and C4 was evident from NMR data. However, in order to prove unequivocally the absolute stereochemistry at C3 and C4, the X-ray structure determinations of (1), (3) and the major isomer of (2) were carried out.

The molecular structures for compounds (1), (2) and (3) are shown in Figs. 1, 2 and 3, respectively. The absolute configuration was clearly established as *β* at C3 and C4. For all compounds, bond distances and angles in the lactam ring are almost identical. However, the four-membered ring is quite planar in compounds (1) and (3) (mean deviations of 0.011 and 0.06 Å, respectively) but slightly bent in (2) (mean deviation of 0.06 Å, dihedral angle 13°). The configuration at the N atom is nearly planar in (1) and (2), while it is more pyramidal in (3), the sum of the three bond angles being 356, 359 and 348°, respectively. The arrangement of the substituents in the vicinity of the lactam ring is similar in (1) and (3), while in (2) the dithiane ring is rotated around the N1—C2′ bond [torsion angle C2—N1—C2′—C1′ 106.4 (5) for (1), −39.5 (4) for (2) and 89.4 (3)° for (3)]. Thus, the C2′—H bond eclipses the N1—C2 bond in compounds (1) and (3) (torsion angle C2—N1—C2′—H2′ −11 and −30°, respectively) while in compound (2) it eclipses the N1—C4 bond (C2—N1—C2′—H2′ −158, C4—N1—C2′—H2′ 9°). In Fig. 4, where the

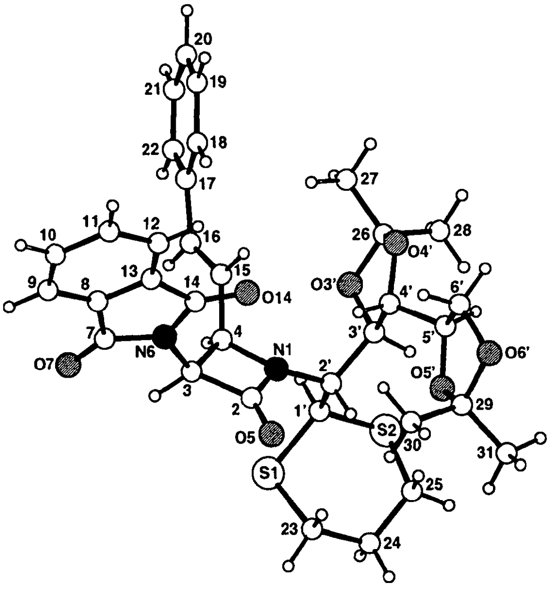


Fig. 1. Perspective view of (1).

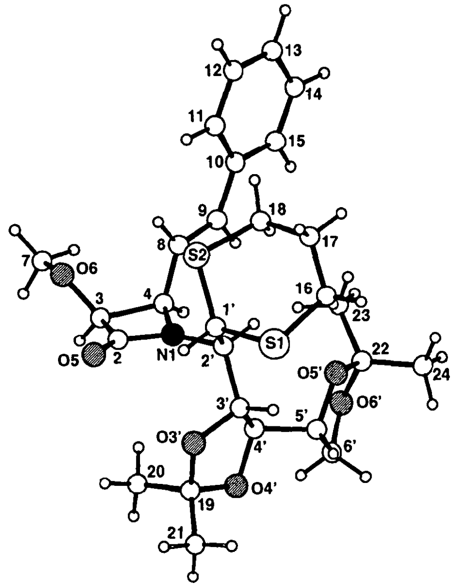


Fig. 2. Perspective view of (2). The disorder of one of the isopropylidene rings (minority position) is not represented.

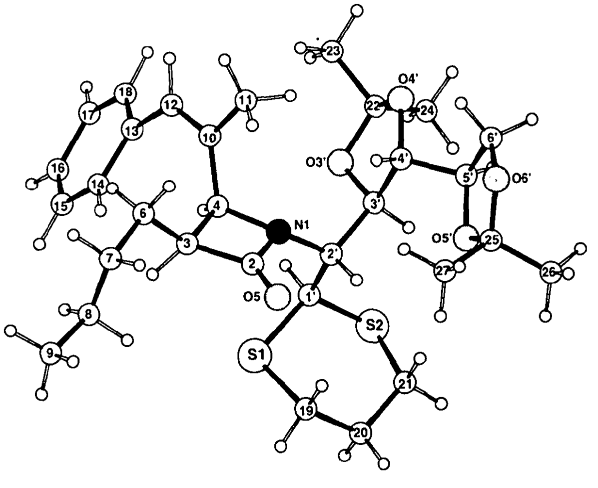


Fig. 3. Perspective view of (3).

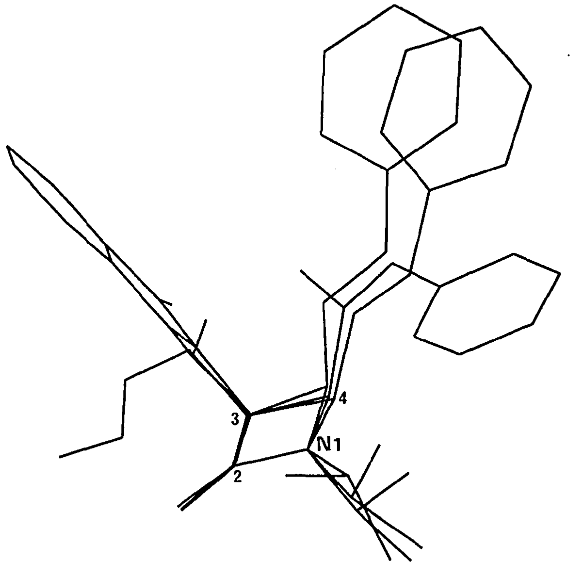


Fig. 4. Superimposition of the three molecules (atoms N1, C2 and C3 are superimposed).

three molecules are superimposed, it can be seen that the orientation of the styryl chain at C4 is very similar in (1) and (2) [torsion angle N1—C4—Cβ—Cα 148.1 (6) for (1), 120.7 (6) for (2) and 152.0 (4)° for (3), Cβ and Cα labelling the double bond], and that there is no steric hindrance between the substituents fixed at C3 and C4.

Experimental

Compound (1)

Crystal data

$C_{34}H_{38}N_2O_7S_2.C_4H_8O_2$
$M_r = 738.92$
Orthorhombic
$P2_12_12_1$
$a = 9.518\ (8)$ Å
$b = 16.941\ (12)$ Å
$c = 24.261\ (18)$ Å
$V = 3912.0\ (51)$ Å^3
$Z = 4$
$D_x = 1.25$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 5.2–40.4°$
$\mu = 1.64$ mm^{-1}
$T = 293$ K
Prism
0.45 × 0.35 × 0.25 mm
Colourless

Data collection

Philips PW100 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3984 measured reflections
3984 independent reflections
2790 observed reflections [$I > 3.0\sigma(I)$]

$\theta_{\max} = 67.85°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 29$
3 standard reflections
frequency: 180 min
intensity variation: none

Refinement

Refinement on F
$R = 0.048$
$wR = 0.064$
$S = 0.95$
2785 reflections
289 parameters
H-atom parameters not refined
Calculated weights $w = 1/[\sigma^2(F) + 0.002932F^2]$

$(\Delta/\sigma)_{\max} = 0.03$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

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

	x	y	z	$U_{\rm eq}$
N1	0.4228 (4)	0.2923 (2)	0.4142 (1)	0.038 (3)
C2	0.5227 (6)	0.2943 (3)	0.4537 (2)	0.050 (5)
C3	0.4234 (6)	0.3323 (3)	0.4954 (2)	0.047 (4)
C4	0.3090 (5)	0.3273 (2)	0.4484 (2)	0.042 (4)
O5	0.6415 (4)	0.2696 (2)	0.4546 (2)	0.069 (4)
N6	0.4629 (4)	0.4085 (2)	0.5174 (1)	0.047 (4)
C7	0.4444 (6)	0.4307 (3)	0.5726 (2)	0.057 (5)
O7	0.3818 (6)	0.3925 (3)	0.6063 (2)	0.092 (6)
C8	0.5122 (6)	0.5094 (3)	0.5782 (2)	0.053 (5)
C9	0.5283 (7)	0.5563 (3)	0.6245 (2)	0.069 (6)
C10	0.6007 (8)	0.6266 (4)	0.6173 (3)	0.080 (7)
C11	0.6535 (8)	0.6486 (4)	0.5666 (3)	0.087 (8)
C12	0.6369 (7)	0.6009 (4)	0.5206 (3)	0.077 (7)
C13	0.5652 (6)	0.5307 (3)	0.5280 (2)	0.054 (5)
C14	0.5356 (6)	0.4666 (3)	0.4883 (2)	0.053 (5)
O14	0.5664 (5)	0.4623 (2)	0.4400 (1)	0.068 (4)
C15	0.2484 (5)	0.4027 (3)	0.4295 (2)	0.044 (4)
C16	0.1139 (6)	0.4221 (3)	0.4383 (2)	0.053 (5)
C17	0.0494 (6)	0.4963 (3)	0.4223 (2)	0.056 (5)
C18	0.1219 (7)	0.5646 (3)	0.4117 (3)	0.070 (6)
C19	0.0562 (8)	0.6312 (4)	0.3927 (3)	0.087 (8)
C20	−0.0854 (9)	0.6319 (5)	0.3830 (3)	0.093 (9)
C21	−0.1611 (8)	0.5654 (5)	0.3940 (4)	0.097 (9)
C22	−0.0971 (6)	0.4990 (4)	0.4140 (3)	0.072 (7)
C1′	0.3129 (5)	0.1750 (2)	0.3713 (2)	0.047 (4)
S1	0.3367 (2)	0.1204 (1)	0.4353 (1)	0.059 (1)
S2	0.3043 (2)	0.1106 (1)	0.3120 (1)	0.066 (1)
C2′	0.4219 (5)	0.2426 (2)	0.3654 (2)	0.038 (4)
C3′	0.4041 (4)	0.2887 (2)	0.3119 (2)	0.037 (4)
O3′	0.2714 (3)	0.3285 (2)	0.3112 (1)	0.043 (3)
C4′	0.5095 (5)	0.3552 (2)	0.3017 (2)	0.042 (4)
O4′	0.4284 (3)	0.4146 (2)	0.2747 (1)	0.057 (3)
C5′	0.6299 (5)	0.3313 (3)	0.2652 (2)	0.050 (4)
O5′	0.6992 (4)	0.2649 (2)	0.2886 (2)	0.063 (4)
C6′	0.7475 (6)	0.3919 (3)	0.2588 (3)	0.069 (6)
O6′	0.8686 (4)	0.3440 (2)	0.2531 (2)	0.068 (4)
C23	0.4945 (7)	0.0676 (3)	0.4213 (2)	0.071 (6)
C24	0.4905 (8)	0.0162 (3)	0.3696 (3)	0.088 (8)
C25	0.4710 (8)	0.0632 (3)	0.3166 (2)	0.079 (7)
C26	0.2854 (5)	0.3880 (3)	0.2701 (2)	0.050 (4)
C27	0.1893 (6)	0.4561 (3)	0.2838 (2)	0.065 (6)
C28	0.2596 (6)	0.3560 (3)	0.2133 (2)	0.065 (6)
C29	0.8485 (5)	0.2773 (3)	0.2883 (2)	0.054 (5)
C30	0.8970 (7)	0.2943 (4)	0.3456 (3)	0.081 (7)
C31	0.9183 (7)	0.2073 (4)	0.2631 (3)	0.082 (7)
C32	0.5131 (10)	0.1401 (6)	0.1664 (4)	0.120 (11)
C33	0.5265 (9)	0.1971 (5)	0.1235 (4)	0.102 (10)
O34	0.6292 (10)	0.2130 (8)	0.1023 (6)	0.353 (29)
O35	0.4143 (6)	0.2314 (4)	0.1058 (2)	0.109 (7)
C36	0.4239 (11)	0.2925 (6)	0.0643 (4)	0.116 (11)
C37	0.2848 (13)	0.3197 (7)	0.0509 (4)	0.147 (15)

Table 2. *Selected geometric parameters* (Å, °) *for compound* (1)

N1—C2	1.351 (6)	C1′—S1	1.821 (4)
N1—C4	1.489 (6)	C1′—S2	1.807 (4)
N1—C2′	1.453 (5)	C1′—C2′	1.552 (6)
C2—C3	1.528 (7)	S1—C23	1.781 (7)
C2—O5	1.206 (7)	S2—C25	1.782 (7)
C3—C4	1.579 (6)	C2′—C3′	1.523 (6)
C3—N6	1.446 (6)	C3′—O3′	1.432 (5)
C4—C15	1.475 (6)	C3′—C4′	1.528 (6)
N6—C7	1.402 (6)	O3′—C26	1.425 (5)
N6—C14	1.394 (6)	C4′—O4′	1.427 (5)
C7—O7	1.203 (7)	C4′—C5′	1.504 (6)
C7—C8	1.487 (7)	O4′—C26	1.438 (6)
C8—C9	1.383 (7)	C5′—O5′	1.421 (6)
C8—C13	1.368 (7)	C5′—C6′	1.527 (7)
C9—C10	1.387 (9)	O5′—C29	1.436 (6)
C10—C11	1.379 (10)	C6′—O6′	1.416 (7)
C11—C12	1.387 (9)	O6′—C29	1.430 (6)
C12—C13	1.382 (8)	C23—C24	1.526 (8)
C13—C14	1.480 (7)	C24—C25	1.524 (9)
C14—O14	1.211 (6)	C26—C27	1.509 (7)
C15—C16	1.339 (7)	C26—C28	1.501 (7)
C16—C17	1.452 (7)	C29—C30	1.492 (8)
C17—C18	1.372 (8)	C29—C31	1.491 (9)
C17—C22	1.409 (8)	C32—C33	1.425 (13)
C18—C19	1.370 (9)	C33—O34	1.136 (14)
C19—C20	1.368 (11)	C33—O35	1.290 (10)
C20—C21	1.364 (11)	O35—C36	1.446 (11)
C21—C22	1.369 (10)	C36—C37	1.439 (16)
C2—N1—C4	96.1 (3)	S1—C1′—C2′	111.8 (3)
C2—N1—C2′	126.7 (4)	S2—C1′—C2′	113.7 (3)
C4—N1—C2′	133.0 (3)	C1′—S1—C23	101.4 (2)
N1—C2—C3	92.6 (4)	C1′—S2—C25	100.5 (3)
N1—C2—O5	131.7 (5)	N1—C2′—C1′	110.8 (3)
C3—C2—O5	135.6 (5)	N1—C2′—C3′	113.4 (3)

C2—C3—C4	85.7 (3)	C1′—C2′—C3′	112.5 (3)
C2—C3—N6	117.3 (4)	C2′—C3′—O3′	110.4 (3)
C4—C3—N6	119.5 (4)	C2′—C3′—C4′	116.3 (3)
N1—C4—C3	85.6 (3)	O3′—C3′—C4′	103.3 (3)
N1—C4—C15	117.1 (4)	C3′—O3′—C26	105.0 (3)
C3—C4—C15	116.7 (4)	C3′—C4′—O4′	103.8 (3)
C3—N6—C7	124.0 (4)	C3′—C4′—C5′	113.4 (4)
C3—N6—C14	125.0 (4)	O4′—C4′—C5′	109.3 (3)
C7—N6—C14	110.8 (4)	C4′—O4′—C26	109.1 (3)
N6—C7—O7	124.6 (5)	C4′—C5′—O5′	109.4 (4)
N6—C7—C8	106.0 (4)	C4′—C5′—C6′	116.0 (4)
O7—C7—C8	129.4 (5)	O5′—C5′—C6′	103.5 (4)
C7—C8—C9	129.7 (5)	C5′—O5′—C29	110.0 (4)
C7—C8—C13	108.3 (4)	C5′—C6′—O6′	102.8 (4)
C9—C8—C13	122.0 (5)	C6′—O6′—C29	106.6 (4)
C8—C9—C10	116.5 (5)	S1—C23—C24	115.0 (4)
C9—C10—C11	121.7 (6)	C23—C24—C25	113.5 (5)
C10—C11—C12	121.2 (6)	S2—C25—C24	113.4 (4)
C11—C12—C13	117.0 (6)	O3′—C26—O4′	104.8 (3)
C8—C13—C12	121.7 (5)	O3′—C26—C27	109.2 (4)
C8—C13—C14	108.4 (4)	O3′—C26—C28	111.9 (4)
C12—C13—C14	129.9 (5)	O4′—C26—C27	108.5 (4)
N6—C14—C13	106.5 (4)	O4′—C26—C28	109.8 (4)
N6—C14—O14	124.6 (4)	C27—C26—C28	112.3 (4)
C13—C14—O14	128.9 (5)	O5′—C29—O6′	104.5 (4)
C4—C15—C16	122.5 (4)	O5′—C29—C30	109.3 (4)
C15—C16—C17	125.0 (5)	O5′—C29—C31	109.1 (4)
C16—C17—C18	124.6 (5)	O6′—C29—C30	111.2 (4)
C16—C17—C22	119.0 (5)	O6′—C29—C31	108.9 (4)
C18—C17—C22	116.3 (5)	C30—C29—C31	113.4 (5)
C17—C18—C19	121.9 (6)	C32—C33—O34	124.6 (10)
C18—C19—C20	121.0 (7)	C32—C33—O35	118.3 (8)
C19—C20—C21	118.7 (7)	O34—C33—O35	117.0 (10)
C20—C21—C22	120.9 (7)	C33—O35—C36	120.2 (7)
C17—C22—C21	121.2 (6)	O35—C36—C37	109.2 (8)
S1—C1′—S2	112.2 (2)		

C4—N1—C2—C3	−1.0 (4)	C24—C25—S2—C1′	61.2 (4)
N1—C2—C3—C4	1.0 (5)	C25—S2—C1′—S1	−59.5 (3)
C2—C3—C4—N1	−0.9 (4)	N1—C2′—C3′—O3′	−62.5 (4)
C3—C4—N1—C2	1.0 (4)	C3′—O3′—C26—O4′	−36.1 (4)
C2′—N1—C4—C15	−84.2 (5)	O3′—C26—O4′—C4′	20.9 (4)
N1—C4—C15—C16	148.1 (6)	C26—O4′—C4′—C3′	1.5 (4)
C4—C15—C16—C17	177.8 (7)	O4′—C4′—C3′—O3′	−23.2 (4)
C15—C16—C17—C18	−20.8 (5)	C4′—C3′—O3′—C26	36.5 (4)
O5—C2—C3—N6	64.5 (5)	S2—C1′—C2′—C3′	51.4 (3)
C4—C3—N6—C14	−68.0 (5)	C1′—C2′—C3′—C4′	−178.4 (5)
C2—C3—N6—C7	−140.4 (6)	C2′—C3′—C4′—C5′	97.2 (4)
C3—N6—C7—O7	−7.7 (5)	C3′—C4′—C5′—C6′	−173.2 (5)
C4—N1—C2′—C3′	83.1 (4)	C4′—C5′—C6′—O6′	147.0 (6)
C2—N1—C2′—C1′	106.4 (5)	C5′—C6′—O6′—C29	−36.2 (5)
N1—C2′—C1′—S1	−52.1 (3)	C6′—O6′—C29—O5′	31.2 (4)
C2′—C1′—S1—C23	−71.8 (3)	O6′—C29—O5′—C5′	−12.8 (4)
S2—C1′—S1—C23	57.2 (3)	C29—O5′—C5′—C6′	−8.8 (4)
C1′—S1—C23—C24	−56.0 (4)	O5′—C5′—C6′—O6′	27.2 (4)
S1—C23—C24—C25	63.4 (5)	O4′—C4′—C5′—C6′	71.5 (4)
C23—C24—C25—S2	−66.1 (5)		

Compound (2)

Crystal data

$C_{27}H_{37}NO_6S_2$
$M_r = 535.72$
Triclinic
$P1$
$a = 9.038\ (4)$ Å
$b = 9.488\ (4)$ Å
$c = 10.443\ (6)$ Å
$\alpha = 92.07\ (3)^\circ$
$\beta = 109.45\ (3)^\circ$
$\gamma = 120.31\ (4)^\circ$
$V = 705.7\ (5)$ Å^3
$Z = 1$
$D_x = 1.26$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 6.2$–40.4°
$\mu = 1.99$ mm^{-1}
$T = 293$ K
Prism
0.53 × 0.25 × 0.25 mm
Colourless

Data collection

Philips PW100 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2562 measured reflections
2562 independent reflections
2393 observed reflections [$I > 3.0\sigma(I)$]

$\theta_{\max} = 67.93^\circ$
$h = -10 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 180 min
intensity variation: none

Refinement

Refinement on F
$R = 0.055$
$wR = 0.075$
$S = 0.90$
2392 reflections
302 parameters
H-atom parameters not refined
Calculated weights $w = 1/[\sigma^2(F) + 0.006768F^2]$

$(\Delta/\sigma)_{\max} = 0.02$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.60$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for compound* (2)

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

	x	y	z	U_{eq}
N1	0.0169 (5)	0.1151 (5)	−0.3070 (4)	0.046 (4)
C2	0.1335 (6)	0.2872 (6)	−0.2684 (5)	0.053 (5)
C3	0.3068 (6)	0.2774 (6)	−0.2317 (5)	0.056 (6)
C4	0.1671 (6)	0.0820 (6)	−0.2527 (5)	0.055 (5)
O5	0.1078 (5)	0.4001 (4)	−0.2653 (4)	0.067 (5)
O6	0.4478 (5)	0.3729 (5)	−0.0990 (4)	0.066 (5)
C7	0.6139 (9)	0.3769 (10)	−0.0762 (7)	0.089 (10)
C8	0.1758 (7)	0.0237 (6)	−0.1222 (5)	0.056 (5)
C9	0.1551 (7)	−0.1243 (7)	−0.1088 (5)	0.064 (7)
C10	0.1517 (6)	−0.1921 (7)	0.0139 (5)	0.058 (6)
C11	0.1676 (9)	−0.1086 (8)	0.1341 (6)	0.078 (8)
C12	0.1652 (11)	−0.1773 (10)	0.2488 (6)	0.093 (10)
C13	0.1462 (10)	−0.3289 (10)	0.2462 (8)	0.093 (10)
C14	0.1270 (9)	−0.4168 (8)	0.1270 (8)	0.085 (9)
C15	0.1331 (7)	−0.3470 (7)	0.0134 (6)	0.067 (6)
C1′	−0.2613 (6)	0.0742 (5)	−0.2804 (4)	0.047 (5)
S1	−0.5159†	−0.0474†	−0.3450†	0.067 (2)
S2	−0.1537 (2)	0.1114 (2)	−0.0917 (2)	0.057 (1)
C2′	−0.1858 (6)	0.0030 (5)	−0.3591 (4)	0.042 (4)
C3′	−0.2798 (6)	−0.0282 (5)	−0.5174 (4)	0.047 (5)
O3′	−0.2191 (6)	0.1296 (4)	−0.5551 (3)	0.068 (5)
C4′	−0.2310 (7)	−0.1187 (6)	−0.6055 (5)	0.055 (6)
O4′	−0.2358 (8)	−0.0468 (6)	−0.7222 (4)	0.098 (7)
C5′	−0.3772 (8)	−0.3064 (6)	−0.6613 (5)	0.068 (7)
O5′	−0.3761 (8)	−0.3818 (5)	−0.5468 (5)	0.101 (8)
C6′	−0.3328 (12)	−0.3952 (8)	−0.7538 (6)	0.094 (11)
O6′	−0.2560 (8)	−0.4664 (8)	−0.6609 (6)	0.060 (1)
O6″	−0.3857 (18)	−0.5509 (16)	−0.7161 (14)	0.064 (3)
C16	−0.5608 (7)	−0.2367 (7)	−0.2858 (7)	0.073 (7)
C17	−0.4692 (9)	−0.2040 (7)	−0.1290 (7)	0.078 (8)
C18	−0.2578 (8)	−0.1021 (8)	−0.0704 (6)	0.074 (7)
C19	−0.1856 (8)	0.1208 (6)	−0.6793 (5)	0.067 (7)
C20	0.0233 (13)	0.2417 (13)	−0.6370 (11)	0.121 (14)
C21	−0.3065 (11)	0.1539 (10)	−0.7932 (6)	0.103 (12)
C22	−0.3372 (8)	−0.5075 (7)	−0.5641 (6)	0.057 (1)
C23	−0.1905 (21)	−0.4750 (19)	−0.4222 (15)	0.099 (4)
C24	−0.5182 (18)	−0.6743 (16)	−0.6198 (14)	0.087 (3)
C23″	−0.1339 (35)	−0.4554 (31)	−0.4931 (26)	0.085 (6)
C24″	−0.4750 (23)	−0.6779 (20)	−0.5501 (18)	0.058 (3)

† Coordinate fixed to define origin.

Table 4. *Selected geometric parameters* (Å, °) *for compound* (2)

N1—C2	1.368 (6)	C2′—C3′	1.521 (6)
N1—C4	1.481 (8)	C3′—O3′	1.434 (6)
N1—C2′	1.453 (7)	C3′—C4′	1.541 (8)
C2—C3	1.536 (9)	O3′—C19	1.435 (7)
C2—O5	1.207 (7)	C4′—O4′	1.417 (6)
C3—C4	1.582 (7)	C4′—C5′	1.514 (7)
C3—O6	1.391 (6)	O4′—C19	1.421 (8)
C4—C8	1.481 (7)	C5′—O5′	1.415 (7)
O6—C7	1.419 (11)	C5′—C6′	1.532 (12)
C8—C9	1.338 (8)	O5′—C22	1.424 (9)
C9—C10	1.457 (7)	C6′—O6′	1.397 (11)
C10—C11	1.384 (9)	C6′—O6″	1.421 (15)
C10—C15	1.392 (8)	O6′—C22	1.394 (10)
C11—C12	1.386 (9)	O6″—C22	1.479 (14)
C12—C13	1.358 (12)	C16—C17	1.504 (9)
C13—C14	1.382 (12)	C17—C18	1.508 (11)
C14—C15	1.383 (9)	C19—C20	1.516 (14)
C1′—S1	1.819 (5)	C19—C21	1.489 (10)
C1′—S2	1.812 (4)	C22—C23	1.515 (17)
C1′—C2′	1.548 (8)	C22—C24	1.486 (16)
S1—C16	1.812 (6)	C22—C23″	1.523 (35)
S2—C18	1.813 (7)	C22—C24″	1.514 (19)
C2—N1—C4	96.1 (4)	C3′—O3′—C19	109.7 (4)
C2—N1—C2′	131.9 (4)	C3′—C4′—O4′	103.1 (4)
C4—N1—C2′	131.1 (4)	C3′—C4′—C5′	112.9 (4)
N1—C2—C3	91.3 (4)	O4′—C4′—C5′	107.4 (5)
N1—C2—O5	133.7 (5)	C4′—O4′—C19	108.8 (5)
C3—C2—O5	135.0 (5)	C4′—C5′—O5′	108.7 (5)
C2—C3—C4	85.7 (4)	C4′—C5′—C6′	112.9 (5)
C2—C3—O6	114.7 (5)	O5′—C5′—C6′	104.5 (6)
C4—C3—O6	118.4 (5)	C5′—O5′—C22	109.7 (5)
N1—C4—C3	85.4 (4)	C5′—C6′—O6′	102.0 (6)
N1—C4—C8	112.6 (4)	C5′—C6′—O6″	103.9 (8)
C3—C4—C8	115.6 (5)	C6′—O6′—C22	109.9 (6)
C3—O6—C7	112.8 (5)	C6′—O6″—C22	103.9 (10)
C4—C8—C9	124.0 (5)	S1—C16—C17	113.4 (5)
C8—C9—C10	126.3 (6)	C16—C17—C18	113.6 (6)
C9—C10—C11	123.0 (6)	S2—C18—C17	114.1 (5)
C9—C10—C15	119.7 (5)	O3′—C19—O4′	106.3 (5)
C11—C10—C15	117.3 (6)	O3′—C19—C20	106.9 (6)
C10—C11—C12	121.0 (7)	O3′—C19—C21	110.6 (5)
C11—C12—C13	120.9 (8)	O4′—C19—C20	109.2 (6)
C12—C13—C14	119.6 (8)	O4′—C19—C21	108.8 (6)
C13—C14—C15	119.6 (7)	C20—C19—C21	114.7 (7)
C10—C15—C14	121.6 (6)	O5′—C22—O6′	103.7 (6)
S1—C1′—S2	111.0 (3)	O5′—C22—O6″	104.4 (7)
S1—C1′—C2′	114.1 (3)	O5′—C22—C23	104.7 (8)
S2—C1′—C2′	113.3 (3)	O5′—C22—C24	107.8 (8)
C1′—S1—C16	101.0 (3)	O5′—C22—C23″	117.5 (12)
C1′—S2—C18	101.5 (3)	O5′—C22—C24″	114.8 (9)
N1—C2′—C1′	109.9 (4)	O6′—C22—C23	109.5 (8)
N1—C2′—C3′	111.5 (4)	O6′—C22—C24	112.1 (8)
C1′—C2′—C3′	112.1 (4)	O6″—C22—C23″	104.8 (13)
C2′—C3′—O3′	109.9 (4)	O6″—C22—C24″	99.4 (10)
C2′—C3′—C4′	115.8 (4)	C23—C22—C24	117.8 (10)
O3′—C3′—C4′	103.4 (4)	C23″—C22—C24″	113.2 (14)
C4—N1—C2—C3	9.9 (5)	C2′—C3′—C4′—C5′	97.7 (5)
N1—C2—C3—C4	−9.3 (5)	C3′—C4′—C5′—C6′	177.7 (7)
C2—C3—C4—N1	8.6 (5)	C3′—C4′—C5′—O5′	−66.8 (5)
C3—C4—N1—C2	−9.7 (5)	C4′—C5′—O5′—C22	−121.4 (7)
C2′—N1—C2—O5	−0.3 (6)	C4′—C5′—C6′—O6′	100.1 (7)
O5—C2—C3—O6	51.4 (6)	C4′—C5′—C6′—O6″	140.8 (10)
C2—C3—O6—C7	−172.6 (7)	S2—C1′—S1—C16	−58.9 (4)
O6—C3—C4—C8	11.6 (5)	C1′—S1—C16—C17	60.4 (4)
C2′—N1—C4—C8	−63.7 (5)	S1—C16—C17—C18	−66.2 (4)
N1—C4—C8—C9	120.7 (6)	C16—C17—C18—S2	65.0 (6)
C4—C8—C9—C10	−176.2 (8)	C17—C18—S2—C1′	−58.2 (4)
C8—C9—C10—C11	0.9 (6)	C18—S2—C1′—S1	57.9 (4)
C8—C9—C10—C15	−178.6 (8)	O3′—C3′—C4′—O4′	−26.5 (5)
C4—N1—C2′—C1′	127.0 (5)	C3′—C4′—O4′—C19	29.6 (5)
C4—N1—C2′—C3′	−108.1 (5)	C4′—O4′—C19—O3′	−21.4 (5)
C2—N1—C2′—C1′	−39.5 (4)	O4′—C19—O3′—C3′	3.0 (5)
C2—N1—C2′—C3′	85.4 (5)	C19—O3′—C3′—C4′	14.5 (4)
N1—C2′—C1′—S1	175.8 (4)	O5′—C5′—C6′—O6′	−17.9 (6)
N1—C2′—C1′—S2	−55.9 (4)	C5′—C6′—O6′—C22	31.2 (7)
N1—C2′—C3′—O3′	−53.3 (4)	C6′—O6′—C22—O5′	−32.2 (6)
N1—C2′—C3′—C4′	63.4 (4)	O6′—C22—O5′—C5′	19.0 (6)
S1—C1′—C2′—C3′	51.3 (4)	C22—O5′—C5′—C6′	−0.6 (6)
S2—C1′—C2′—C3′	179.6 (5)	O5′—C5′—C6′—O6″	22.9 (8)
C1′—C2′—C3′—O3′	70.4 (4)	C5′—C6′—O6″—C22	−35.4 (10)
C1′—C2′—C3′—C4′	−173.0 (6)	C6′—O6″—C22—O5′	35.5 (10)
C2′—C3′—C4′—O4′	−146.7 (6)	O6″—C22—O5′—C5′	−21.0 (7)

Compound (3)

Crystal data

$C_{31}H_{45}NO_5S_2$
$M_r = 575.83$
Orthorhombic
$P2_12_12_1$
$a = 10.770$ (7) Å
$b = 14.355$ (10) Å
$c = 20.690$ (15) Å
$V = 3198.7$ (38) Å^3
$Z = 4$
$D_x = 1.20$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 24 reflections
$\theta = 3.8$–20.1°
$\mu = 0.19$ mm^{-1}
$T = 293$ K
Prism
0.50 × 0.40 × 0.25 mm
Colourless

Data collection

Philips PW100 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
6044 measured reflections
5651 independent reflections
4412 observed reflections [$I > 3.0\sigma(I)$]

$\theta_{\max} = 28.00°$
$h = -12 \rightarrow 25$
$k = -4 \rightarrow 17$
$l = -1 \rightarrow 24$
3 standard reflections
frequency: 180 min
intensity variation: none

Refinement

Refinement on F
$R = 0.052$
$wR = 0.061$
$S = 0.62$
4400 reflections
352 parameters
H-atom parameters not refined
Calculated weights $w = 1/[\sigma^2(F) + 0.000362F^2]$

$(\Delta/\sigma)_{\max} = 0.02$
$\Delta\rho_{\max} = 0.64$ e Å^{-3}
$\Delta\rho_{\min} = -0.76$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystalography* (1974, Vol. IV, Table 2.2B)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for comound* (3)

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

	x	y	z	$U_{\rm eq}$
N1	0.7755 (2)	0.6967 (2)	0.2882 (1)	0.040 (3)
C2	0.7270 (3)	0.7513 (2)	0.3370 (2)	0.046 (4)
C3	0.6261 (3)	0.7914 (3)	0.2938 (2)	0.047 (4)
C4	0.6860 (3)	0.7312 (2)	0.2390 (2)	0.040 (3)
O5	0.7569 (3)	0.7574 (2)	0.3928 (1)	0.072 (3)
C6	0.6048 (4)	0.8958 (3)	0.2867 (2)	0.059 (4)
C7	0.5271 (6)	0.9366 (3)	0.3373 (4)	0.120 (9)
C8	0.4329 (7)	0.9026 (4)	0.3694 (4)	0.144 (11)
C9	0.3519 (6)	0.9519 (5)	0.4143 (4)	0.125 (9)
C10	0.7390 (3)	0.7840 (2)	0.1821 (2)	0.043 (3)
C11	0.8575 (4)	0.8366 (3)	0.1927 (2)	0.054 (4)
C12	0.6842 (3)	0.7857 (3)	0.1247 (2)	0.045 (4)
C13	0.5697 (3)	0.7392 (2)	0.1030 (2)	0.043 (3)
C14	0.4625 (3)	0.7317 (3)	0.1406 (2)	0.049 (4)

C15	0.3582 (3)	0.6872 (3)	0.1174 (2)	0.057 (4)
C16	0.3562 (4)	0.6507 (3)	0.0563 (2)	0.064 (5)
C17	0.4602 (4)	0.6589 (3)	0.0176 (2)	0.064 (5)
C18	0.5638 (3)	0.7034 (3)	0.0409 (2)	0.054 (4)
C1′	0.7224 (3)	0.5290 (2)	0.2922 (2)	0.041 (3)
S1	0.5850 (1)	0.5534 (1)	0.3390 (1)	0.059 (1)
S2	0.7774 (1)	0.4107 (1)	0.3056 (1)	0.053 (1)
C2′	0.8258 (3)	0.6038 (2)	0.2989 (2)	0.038 (3)
C3′	0.9342 (3)	0.5797 (2)	0.2551 (2)	0.039 (3)
O3′	0.8948 (2)	0.5823 (2)	0.1895 (1)	0.047 (2)
C4′	1.0461 (3)	0.6447 (3)	0.2560 (2)	0.043 (3)
O4′	1.0859 (2)	0.6473 (2)	0.1902 (1)	0.062 (3)
C5′	1.1512 (3)	0.6120 (3)	0.2984 (2)	0.052 (4)
O5′	1.1036 (3)	0.5987 (2)	0.3624 (1)	0.070 (3)
C6′	1.2550 (4)	0.6821 (4)	0.3080 (2)	0.077 (5)
O6′	1.2491 (7)	0.7045 (5)	0.3695 (2)	0.228 (12)
C19	0.6438 (4)	0.5352 (4)	0.4206 (2)	0.073 (5)
C20	0.6962 (5)	0.4394 (3)	0.4321 (2)	0.073 (5)
C21	0.8072 (4)	0.4150 (3)	0.3912 (2)	0.066 (5)
C22	1.0050 (3)	0.5895 (3)	0.1524 (2)	0.052 (4)
C23	0.9761 (4)	0.6398 (4)	0.0898 (2)	0.073 (5)
C24	1.0626 (4)	0.4963 (4)	0.1412 (2)	0.078 (6)
C25	1.1741 (5)	0.6513 (4)	0.4071 (2)	0.083 (6)
C26	1.2475 (7)	0.5894 (7)	0.4497 (3)	0.157 (12)
C27	1.0891 (10)	0.7116 (7)	0.4447 (4)	0.175 (14)

Table 6. *Selected geometric parameters* (Å, °) *for compound* (3)

N1—C2	1.380 (5)	C1′—C2′	1.554 (5)
N1—C4	1.487 (4)	S1—C19	1.821 (5)
N1—C2′	1.456 (4)	S2—C21	1.800 (4)
C2—C3	1.520 (5)	C2′—C3′	1.517 (5)
C2—O5	1.202 (5)	C3′—O3′	1.424 (4)
C3—C4	1.564 (5)	C3′—C4′	1.525 (5)
C3—C6	1.523 (5)	O3′—C22	1.416 (4)
C4—C10	1.512 (5)	C4′—O4′	1.428 (4)
C6—C7	1.462 (8)	C4′—C5′	1.506 (5)
C7—C8	1.307 (10)	O4′—C22	1.434 (5)
C8—C9	1.457 (10)	C5′—O5′	1.433 (5)
C10—C11	1.499 (5)	C5′—C6′	1.517 (6)
C10—C12	1.326 (5)	O5′—C25	1.414 (6)
C12—C13	1.472 (5)	C6′—O6′	1.312 (7)
C13—C14	1.397 (5)	O6′—C25	1.357 (9)
C13—C18	1.385 (5)	C19—C20	1.505 (7)
C14—C15	1.378 (5)	C20—C21	1.505 (7)
C15—C16	1.369 (6)	C22—C23	1.516 (6)
C16—C17	1.382 (6)	C22—C24	1.493 (6)
C17—C18	1.373 (6)	C25—C26	1.481 (10)
C1′—S1	1.803 (3)	C25—C27	1.480 (11)
C1′—S2	1.820 (3)		
C2—N1—C4	93.8 (3)	N1—C2′—C1′	110.7 (3)
C2—N1—C2′	123.4 (3)	N1—C2′—C3′	113.9 (3)
C4—N1—C2′	130.5 (3)	C1′—C2′—C3′	109.9 (3)
N1—C2—C3	93.2 (3)	C2′—C3′—O3′	109.5 (3)
N1—C2—O5	129.9 (3)	C2′—C3′—C4′	117.5 (3)
C3—C2—O5	136.8 (4)	O3′—C3′—C4′	103.3 (3)
C2—C3—C4	85.5 (3)	C3′—O3′—C22	105.6 (2)
C2—C3—C6	122.5 (3)	C3′—C4′—O4′	104.0 (3)
C4—C3—C6	122.4 (3)	C3′—C4′—C5′	114.2 (3)
N1—C4—C3	87.4 (2)	O4′—C4′—C5′	109.8 (3)
N1—C4—C10	117.1 (3)	C4′—O4′—C22	108.8 (3)
C3—C4—C10	116.3 (3)	C4′—C5′—O5′	108.1 (3)
C3—C6—C7	114.3 (4)	C4′—C5′—C6′	115.1 (3)
C6—C7—C8	131.2 (6)	O5′—C5′—C6′	103.3 (3)
C7—C8—C9	127.4 (7)	C5′—O5′—C25	109.9 (3)
C4—C10—C11	117.4 (3)	C5′—C6′—O6′	104.7 (4)
C4—C10—C12	122.6 (3)	C6′—O6′—C25	116.5 (6)
C11—C10—C12	120.1 (3)	S1—C19—C20	114.1 (3)
C10—C12—C13	129.7 (3)	C19—C20—C21	114.9 (4)
C12—C13—C14	123.8 (3)	S2—C21—C20	114.8 (3)
C12—C13—C18	119.4 (3)	O3′—C22—O4′	104.9 (3)
C14—C13—C18	116.8 (3)	O3′—C22—C23	109.0 (3)
C13—C14—C15	121.0 (3)	O3′—C22—C24	111.5 (3)
C14—C15—C16	120.8 (4)	O4′—C22—C23	108.4 (3)
C15—C16—C17	119.3 (4)	O4′—C22—C24	110.5 (3)
C16—C17—C18	119.7 (4)	C23—C22—C24	112.3 (4)
C13—C18—C17	122.4 (4)	O5′—C25—O6′	104.2 (5)
S1—C1′—S2	111.5 (2)	O5′—C25—C26	110.8 (5)
S1—C1′—C2′	114.0 (2)	O5′—C25—C27	108.9 (5)
S2—C1′—C2′	113.5 (2)	O6′—C25—C26	111.1 (6)
C1′—S1—C19	100.6 (2)	O6′—C25—C27	110.0 (6)
C1′—S2—C21	100.1 (2)	C26—C25—C27	111.6 (6)
C4—N1—C2—C3	1.8 (3)	C2′—C3′—C4′—C5′	98.0 (4)
N1—C2—C3—C4	−1.7 (4)	C3′—C4′—C5′—C6′	−171.2 (4)
C2—C3—C4—N1	1.6 (3)	C3′—C4′—C5′—O5′	−56.3 (3)
C3—C4—N1—C2	−1.8 (3)	S2—C1′—S1—C19	60.1 (2)
C2′—N1—C4—C10	−101.9 (4)	C1′—S1—C19—C20	−58.0 (3)
N1—C4—C10—C11	−28.7 (3)	S1—C19—C20—C21	62.4 (4)
N1—C4—C10—C12	152.0 (4)	C19—C20—C21—S2	−63.5 (4)
C3—C4—C10—C12	−106.7 (4)	C20—C21—S2—C1′	58.7 (3)
C4—C10—C12—C13	−1.5 (3)	C21—S2—C1′—S1	−60.3 (2)
C10—C12—C13—C14	40.3 (4)	N1—C2′—C3′—O3′	−61.2 (3)
C10—C4—C3—C6	8.6 (3)	C2′—C3′—O3′—C22	161.5 (4)
C4—C3—C6—C7	168.9 (5)	C4′—C3′—O3′—C22	35.6 (3)
C2—C3—C6—C7	−83.9 (5)	C3′—O3′—C22—O4′	−35.9 (3)
C3—C6—C7—C8	−33.9 (5)	O3′—C22—O4′—C4′	21.5 (3)
C6—C7—C8—C9	−172.6 (10)	C22—O4′—C4′—C3′	0.3 (3)
C4—N1—C2′—C1′	−42.5 (3)	O4′—C4′—C3′—O3′	−21.7 (3)
C4—N1—C2′—C3′	82.0 (3)	O4′—C4′—C5′—C6′	72.5 (4)
C2—N1—C2′—C1′	89.4 (3)	O5′—C5′—C6′—O6′	−4.5 (4)
C2—N1—C2′—C3′	−146.1 (4)	C5′—C6′—O6′—C25	10.8 (5)
N1—C2′—C1′—S1	−50.3 (3)	C6′—O6′—C25—O5′	−12.4 (5)
N1—C2′—C1′—S2	−179.4 (3)	O6′—C25—O5′—C5′	8.4 (4)
S2—C1′—C2′—C3′	53.8 (3)	C25—O5′—C5′—C6′	−2.5 (4)
C1′—C2′—C3′—C4′	−179.0 (4)		

The absolute configuration was established for all three compounds by comparison of selected Bijvoet pairs and agrees with the known configuration, C2′(*R*), of the sugar moiety. In (1), a molecule of solvent (ethyl acetate) was found, in which the ketonic O atom O34 exhibits very high anisotropic thermal motion. In (2), one of the isopropylidene rings is disordered. This ring adopts an envelope conformation where atom O6′ occupies two positions up and down the mean plane: the adjacent dimethyl groups on C6′ are split. Occupancy factors were refined and fixed at $\frac{2}{3}$ and $\frac{1}{3}$. In (3), atom O6′ exhibits very high anisotropic thermal motion but no splitting of the methyl groups on C6′ was observed. Isotropic temperature factors of the H atoms were set equal to $1.10U_{\rm eq}$ of the bonded C atom. Data collection: Philips PW1100/20 software. Data reduction: *PHIL* (Riche, 1981). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *R3M* (Riche, 1983); *ORTEP* (Johnson, 1963). Software used to prepare material for publication: *ACTACIF* (Riche, 1992).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: PA1106). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). **C50**, 1480–1482

Ethyl 9-Adeninylacetate at 122 K

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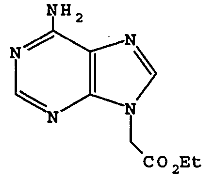
(*Received* 24 *March* 1994; *accepted* 25 *April* 1994)

Abstract

The structure of the title compound, $C_9H_{11}N_5O_2$, at 122 K has been established by X-ray diffraction methods. The ethyl acetate moiety is virtually planar and almost perpendicular to the adenine ring system. Hydrogen bonds between the amino groups and two adenine N atoms connect the molecules in chains parallel to the *c* axis.

Comment

The title compound, (I), was isolated as a reaction intermediate in the preparation of the building blocks of PNA, the peptide analogue of DNA (Nielsen, Egholm, Berg & Buchardt, 1991; Egholm, Buchardt, Nielsen & Berg, 1992). Details of the preparation of the compound will be published elsewhere (Egholm *et al.*, 1994). The structure determination was undertaken to establish where the substitution in the adenine ring had occurred and to elucidate how a bulky substituent influences the hydrogen-bonding pattern. The molecular geometry is illustrated in Fig. 1 and by the bond lengths and angles in Table 2; these values are in excellent agreement with those found in other structures containing the adenine ring system (Stewart & Jensen, 1964; Lai & Marsh, 1972; Wilson, Tollin & Howie, 1986; Low, Tollin & Howie, 1987).



(I)

The structure determination revealed that the substitution had occurred at the 9 position. The ethyl acetate fragment adopts an extended conformation. The six atoms of this moiety are coplanar with a maximum deviation from the least-squares plane of 0.041 (1) Å for O31. This plane is almost perpendicular to the least-squares plane defined by the adenine ring system, the angle between the two planes being 84.46 (4)°, and the torsion angle C8—C9—C22—C21 being 104.65 (13)°. This conformation differs significantly from the one found for other substituents in this position; in adenosine (Lai & Marsh, 1972) the equivalent torsion angle is 9.9°. The two H atoms of the amine group are potential hydrogen-bond donors and as well as atoms N1, N3 and N7 of the adenine ring, O21 of the ethyl acetate fragment could also be a hydrogen-bond acceptor. However, the hydrogen-bonding pattern is similar to that found in 9-methyl adenine (Stewart & Jensen, 1964) with N16—H162···N1 and N16—H161···N7 hydrogen bonds connecting molecules related by translational symmetry along the *c* axis (Table 2, Fig. 2). The plane through the adenine ring is almost parallel to the *ab* plane and the side chains are oriented so that they fill the space between the adenine ring planes of neighbouring molecules.

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