Table 10. *Distances* (Å) *and angles* (°) *for possible intra- and intermolecular hydrogen-bond contacts*

	$D\cdots A$	$H\cdots A$	$\angle D-H\cdots A$
(*a*) AICA.C_3H_7OH			
O(10)–H(10)···O(7)$[1-x, -\frac{1}{2}+y, 1\frac{1}{2}-z]$	2·737 (7)	1·957 (7)	150·0 (10)
N(1)–H(1)···O(10)$[1-x, -y, 1-z]$	2·804 (7)	1·870 (7)	162·7 (10)
N(9)–H(91)···N(3)$[x, 1+y, z]$	3·199 (6)	2·398 (6)	161·8 (9)
N(8)–H(81)···N(3)$[-x, -1-y, 1-z]$	3·184 (6)	2·374 (6)	148·7 (9)
N(8)–H(81)···N(3)$[x,y,z]$	2·802 (6)	2·379 (6)	108·5 (9)
N(9)–H(92)···O(7)$[x,y,z]$	3·042 (6)	2·493 (6)	120·0 (9)
(*b*) AICA.H_2O			
O(10)–H(101)···N(1)$[1-x, -y, 1-z]$	2·910 (4)	1·96 (5)	180 (5)
O(10)–H(102)···N(9)$[x,y,z]$	2·966 (4)	2·02 (5)	155 (5)
N(3)–H(3)···O(7)$[\frac{1}{2}-x, \frac{1}{2}+y, -z]$	2·847 (4)	1·90 (5)	161 (5)
N(8)–H(81)···O(10)$[1-x, -y, -z]$	2·857 (4)	1·94 (5)	157 (5)
N(8)–H(82)···O(7)$[\frac{1}{2}-x, \frac{1}{2}+y, -z]$	2·945 (4)	1·97 (5)	163 (5)
N(9)–H(91)···N(1)$[-x, -y, 1-z]$	3·298 (4)	2·30 (5)	175 (5)
C(2)–H(2)···O(10)$[-\frac{1}{2}+x, \frac{1}{2}-y, z]$	3·261 (4)	2·37 (5)	147 (5)
N(9)–H(92)···O(7)$[x,y,z]$	3·008 (4)	2·40 (5)	121 (5)
(*c*) HAICA$^+$.$H_2PO_4^-$			
O(12)–H(12)···O(14)$[2-x, \frac{1}{2}+y, \frac{1}{2}-z]$	2·610 (6)	1·541 (6)	142·5 (9)
O(11)–H(11)···O(14)$[2-x, -\frac{1}{2}+y, \frac{1}{2}-z]$	2·638 (6)	1·607 (6)	132·8 (9)
N(1)–H(1)···O(13)$[1-x, \frac{1}{2}+y, \frac{1}{2}-z]$	2·769 (7)	1·685 (7)	152·8 (10)
N(3)–H(3)···O(13)$[1-x, -y, 1-z]$	2·777 (7)	1·711 (7)	161·5 (10)
N(8)–H(81)···O(7)$[1-x, -1-y, 1-z]$	2·948 (8)	1·834 (8)	171·3 (11)
N(8)–H(82)···O(13)$[1-x, -y, 1-z]$	2·967 (8)	2·181 (7)	123·3 (11)
N(9)–H(91)···O(7)$[x,y,z]$	2·897 (8)	2·174 (8)	129·1 (11)
N(9)–H(92)···O(7)$[1-x, \frac{1}{2}+y, \frac{1}{2}-z]$	2·830 (8)	2·438 (8)	103·2 (11)

Intermolecular hydrogen bonding

Since the three-dimensional hydrogen-bond networks of the three AICA forms have already been reported in detail along with those of the analogous 1,2,3-triazoles (Kálmán, Párkányi, Schawartz & Simon, 1978) only the distances and angles for possible hydrogen-bonded contacts are presented (Table 10).

References

ADAMIAK, D. A. & SAENGER, W. (1979). *Acta Cryst.* B**35**, 924–928.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

FREEMAN, H. C. & HUTCHINSON, N. D. (1979). *Acta Cryst.* B**35**, 2051–2054.

GILLESPIE, R. J. (1963). *J. Chem. Educ.* **40**, 295–301.

HENDERSON, J. F. & PATERSON, A. R. P. (1973). *Nucleotide Metabolism*, p. 103. New York: Academic Press.

KÁLMÁN, A. (1971). *J. Chem. Soc. A*, pp. 1857–1859.

KÁLMÁN, A., PÁRKÁNYI, L., SCHAWARTZ, J. & SIMON, K. (1978). Proc. Symp. Org. Cryst. Chem., Poznań-Dymaczewo, 30 July, pp. 155–193.

KÁLMÁN, A. & SIMON, K. (1975). *Acta Cryst.* A**31**, S175.

KÁLMÁN, A., SIMON, K., SCHAWARTZ, J. & HORVÁTH, G. (1974). *J. Chem. Soc. Perkin Trans.* 2, pp. 1849–1852.

LEMPERT, K., NYITRAI, J., ZAUER, K., KÁLMÁN, A., ARGAY, GY., DUISENBERG, A. J. M. & SOHÁR, P. (1973). *Tetrahedron*, **29**, 3565–3569.

PÁRKÁNYI, L., KÁLMÁN, A., ARGAY, GY. & SCHAWARTZ, J. (1977). *Acta Cryst.* B**33**, 3102–3106.

SCHAWARTZ, J. & HORNYÁK (née HÁMORI), M. (1971). Hungarian Patent No. 164397.

SHELDRICK, G. M. (1976). *SHELX*. A program for crystal structure determination. Univ. of Cambridge, England.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

SZEPESHÁZI, K., LAPIS, K., JENEY, A., SZENDE, B., SCHAWARTZ, J., UJHELYI, E., TAKÁCS, J., KOVALSZKY, I. & TOMPA, A. (1978). *Exp. Pathol.* **15**, 271–287.

ZIMMERMAN, T. P. (1979). *Biochem. Pharmacol.* **28**, 2533–2539.

Acta Cryst. (1980). B**36**, 2328–2333

The Stereochemistry of 3′-*N*-Substituted 3′-Deoxyadenosines

BY W. S. SHELDRICK* AND M. MORR

Gesellschaft für Biotechnologische Forschung mbH, Mascheroder Weg 1, *D*-3300 *Braunschweig-Stöckheim, Federal Republic of Germany*

(*Received* 19 *March* 1980; *accepted* 30 *May* 1980)

Abstract

The crystal structures of three 3′-*N*-substituted 3′-deoxyadenosines have been determined. The antitumor agent from *Helminthosporium* s.p. 215, 3′-amino-3′-deoxyadenosine (I), crystallizes in the monoclinic space group $P2_1$, with $a = 11{\cdot}925\ (3)$, $b = 10{\cdot}302\ (2)$, $c = 4{\cdot}752\ (1)$ Å, $\beta = 100{\cdot}52\ (2)°$, $Z = 2$; 3′-cyclobutylamino-3′-deoxyadenosine (II) crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 11{\cdot}392\ (2)$, $b = 18{\cdot}434\ (2)$, $c = 7{\cdot}992\ (1)$ Å, $Z = 4$; and the oxazolidine (III) of 3′-(*N*-benzyl-*N*-methylamino)-3′-deoxyadenosine crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 9{\cdot}927\ (2)$, $b = 22{\cdot}401\ (4)$, $c = 7{\cdot}743\ (1)$ Å, $Z = 4$. The structures were refined to $R = 0{\cdot}034$, 0·057, and 0·044 for 1108,

---

* To whom correspondence should be addressed.

0567-7408/80/102328-06$01.00

1552, and 1880 reflexions for (I)–(III) respectively. The conformation at the glycosidic torsion angle is *anti* in all three derivatives with respective values of 10·0 (2), 16·5 (3) and −1·3 (2)° for $\chi_{\rm CN}$. Whereas the position of the C(5′)—O(5′) bond relative to the ribose ring is *gauche–gauche* in (II) and (III), a *gauche–trans* conformation is observed in (I). N(3′) is intermolecularly hydrogen bonded through N···H—O bonds to O(2′) in (I) but is not involved in such bonding in (II) and (III). The N(3′) protons in (I) and (II) do not participate in hydrogen bonding. Adenine base stacking is only observed for (I). Here it is of the translation mode with no base overlap.

Introduction

3′-Amino-3′-deoxyadenosine (I), an essential partial structure of the broad-spectrum antibiotic puromycin, is an antitumor agent which has been isolated from the culture filtrate of *Helminthosporium* s.p. 215 (Gerber & Lechevalier, 1962). The inhibitory effect of puromycin on the assembly of polypeptide chains in the ribosomes is believed to be due, in part, to its structural similarity to the terminal 3′-aminoacyladenylate on the transfer RNA and to the ability of the amide proton on N(3′) to hydrogen bond to the active site of the ribosomal enzyme, peptide synthetase. An X-ray structural analysis of puromycin (Sundaralingam & Arora, 1969) showed the molecule to display an elongated conformation with the amide N(3′) involved in one hydrogen bond, of the type N—H···O, to a water of crystallization.

We have recently synthesized a series of 3′-*N*-substituted 3′-deoxyadenosines (Morr & Ernst, 1979) and, to provide more information concerning the preferred molecular conformation of such derivatives and the proclivity of N(3′) to participate in hydrogen bonding, have carried out X-ray structural analyses on representative species. We report here the structures of the antibiotic 3′-amino-3′-deoxyadenosine (I), 3′-cyclobutylamino-3′-deoxyadenosine (II) and the oxazolidine of 3′-(*N*-benzyl-*N*-methylamino)-3′-deoxyadenosine (III). This series allows a comparative study of the following structural aspects: (1) the effect of bulky substituents on N(3′) or the formation of an oxazolidine ring upon the nucleoside conformation; and (2) a comparison of the hydrogen bonding to N(3′) in derivatives which have respectively two (I), one (II), or zero (III) N(3′) protons.

Experimental

Crystals of (I) were obtained on cooling a saturated aqueous solution, crystals of (II) and (III) by cooling saturated methanol solutions. Crystal and refinement data for (I)–(III) are summarized in Table 1. Cell parameters were determined by least squares from the settings for 15 reflexions (±*hkl*) on a Syntex $P2_1$ four-circle diffractometer. Intensities were collected with graphite-monochromated Cu $K\alpha$ radiation (λ = 1·54178 Å). Measurements were carried out in the θ–2θ mode at scan speeds varying linearly between 2·02° min^{-1} (for 150 counts s^{-1} and below) and 11·72° min^{-1} (for 4000 counts s^{-1} and above). The angular 2θ range traversed was from 1·1° below the $K\alpha_1$ to 1·1° above the $K\alpha_2$ reflexion. The net intensity of each reflexion (scaled to counts per minute) was assigned a standard deviation, based on the counting statistics, of $\sigma(I) = t(N_s + N_b)^{1/2}$, where t is the scan rate, N_s the gross count and N_b the total background count. Lorentz and polarization corrections were applied, but no correction was made for absorption. Only those reflexions with $F \geq 3{\cdot}0\sigma(F)$ were retained in the refinements.

Table 1. *Crystal and refinement data*

Compound	(I)	(II)	(III)
Stoichiometry	$C_{10}H_{14}N_6O_3$	$C_{14}H_{20}N_6O_3.CH_3OH$	$C_{18}H_{20}N_6O_3$
Space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	11·925 (3)	11·392 (2)	9·927 (2)
b (Å)	10·302 (2)	18·434 (2)	22·401 (4)
c (Å)	4·752 (1)	7·992 (1)	7·743 (1)
β (°)	100·52 (2)		
U (Å^3)	573·9 (2)	1678·3 (3)	1721·8 (5)
Z	2	4	4
M_r	266·3	352·4	368·4
D_c (Mg m^{-3})	1·54	1·39	1·42
Radiation	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
μ(mm^{-1})	0·89	0·68	0·74
2θ range (°)	3·5–140·0	3·5–135·0	3·5–145·0
F rejection criterion	$<3{\cdot}0\sigma(F)$	$<3{\cdot}0\sigma(F)$	$<3{\cdot}0\sigma(F)$
Number of reflexions	1108	1552	1180
R	0·034	0·057	0·044
$R_w(=\sum w^{1/2}\Delta/\sum w^{1/2}F_o)$	0·035	0·055	0·046
k	1·0	0·4741	2·6700
g	0·0001	0·0002	0·0002
Largest shift/e.s.d.*	0·014	0·129	0·136
Highest peak in difference map (e Å^{-3})*	0·15	0·35	0·17

* Refers to the last refinement cycle.

Structure solution and refinement

All reflexions were included in the direct-methods structure solutions, those with $I \geq 1{\cdot}0\sigma(I)$ being assigned a value of $0{\cdot}25\sigma(I)$. The structures were solved by multisolution tangent refinement (*SHELX*, G. M. Sheldrick) and refined by blocked full-matrix least squares, $\sum w\Delta^2$ being minimized. Difference syntheses revealed the presence of one disordered methanol molecule in (II). In the final cycles fixed site-occupation factors of 0·63 and 0·37 were employed for the two sites of the disordered methanol. A joint isotropic temperature factor which refined to 0·36 with respective e.s.d.'s of 0·01 and 0·03 Å^2 was assigned to the methanol C and C′: otherwise all

Table 2. *Positional parameters* ($\times 10^4$) *for non-hydrogen atoms*

	x	*y*	*z*
Compound (I)			
N(1)	−1821 (2)	−2037 (2)	−2707 (5)
C(2)	−2699 (2)	−1866 (3)	−4875 (6)
N(3)	−2947 (2)	−831 (2)	−6553 (5)
C(4)	−2150 (2)	99 (2)	−5840 (5)
C(5)	−1209 (2)	66 (2)	−3639 (5)
C(6)	−1050 (2)	−1074 (2)	−1992 (5)
N(6)	−194 (2)	−1263 (2)	212 (5)
N(7)	−588 (2)	1203 (2)	−3595 (4)
C(8)	−1157 (2)	1886 (3)	−5713 (5)
N(9)	−2109 (2)	1275 (2)	−7152 (4)
C(1)′	−2946 (2)	1722 (2)	−9619 (5)
O(1)′	−2542 (1)	2856 (2)	−10738 (3)
C(2)′	−4088 (2)	2063 (2)	−8770 (5)
C(3)′	−3908 (2)	3495 (2)	−8003 (5)
C(4)′	−3224 (2)	3962 (2)	−10217 (5)
O(2)′	−4966 (2)	1962 (2)	−11217 (5)
N(3)′	−4943 (2)	4263 (2)	−8022 (5)
C(5)′	−2447 (2)	5100 (3)	−9380 (6)
O(5)′	−1818 (2)	5339 (2)	−11595 (4)
Compound (II)			
N(1)	11988 (3)	843 (2)	5072 (4)
C(2)	11304 (4)	1404 (2)	5454 (5)
N(3)	10492 (3)	1729 (2)	4549 (4)
C(4)	10434 (3)	1423 (2)	3002 (4)
C(5)	11082 (3)	851 (2)	2425 (5)
C(6)	11903 (3)	543 (2)	3515 (5)
N(6)	12593 (3)	−21 (2)	3174 (4)
N(7)	10761 (3)	685 (2)	771 (4)
C(8)	9944 (3)	1160 (2)	437 (5)
N(9)	9693 (3)	1622 (2)	1723 (4)
C(1)′	8859 (4)	2229 (2)	1813 (5)
O(1)′	8051 (2)	2168 (2)	468 (4)
C(2)′	9452 (3)	2961 (2)	1664 (5)
O(2)′	8736 (3)	3497 (1)	2372 (4)
C(3)′	9428 (3)	3072 (2)	−263 (5)
C(4)′	8234 (3)	2761 (2)	−693 (5)
C(5)′	8082 (4)	2485 (2)	−2458 (6)
O(5)′	8902 (3)	1923 (2)	−2778 (4)
N(3)′	9577 (3)	3801 (2)	−895 (4)
C(31)′	10735 (4)	4119 (2)	−681 (6)
C(32)′	10897 (4)	4897 (3)	−1353 (8)
C(33)′	11763 (5)	5036 (3)	88 (9)
C(34)′	11193 (5)	4396 (3)	1054 (7)
O	9814 (5)	3976 (3)	5322 (7)
O′	9824 (8)	3472 (5)	5506 (10)
C	10989 (18)	3630 (14)	5393 (39)
C′	11095 (21)	3295 (26)	5506 (77)
Compound (III)			
N(1)	7736 (3)	774 (1)	14348 (3)
C(2)	7362 (3)	1327 (1)	14789 (3)
N(3)	6655 (2)	1723 (1)	13898 (3)
C(4)	6351 (2)	1512 (1)	12314 (3)
C(5)	6702 (3)	958 (1)	11663 (3)
C(6)	7385 (3)	567 (1)	12769 (3)
N(6)	7700 (3)	3 (1)	12378 (3)
N(7)	6245 (2)	897 (1)	9981 (3)
C(8)	5621 (3)	1403 (1)	9660 (3)
N(9)	5656 (2)	1796 (1)	11020 (3)
C(1)′	4920 (3)	2369 (1)	11191 (3)
O(1)′	4180 (2)	2459 (1)	9688 (3)
C(2)′	5875 (3)	2892 (1)	11433 (3)
O(2)′	5308 (3)	3323 (1)	12570 (3)
C(3)′	5917 (2)	3203 (1)	9659 (3)
C(4)′	4683 (3)	2962 (1)	8702 (3)
C(5)′	4942 (3)	2774 (1)	16853 (4)
O(5)′	6124 (3)	2426 (1)	16802 (3)
N(3)′	5795 (2)	3842 (1)	10038 (3)
C(31)′	4970 (3)	3846 (1)	11573 (4)
C(32)′	7117 (3)	4122 (1)	10269 (4)
C(33)′	7089 (3)	4795 (1)	10298 (4)
C(34)′	5961 (3)	5128 (1)	9938 (5)
C(35)′	6023 (4)	5746 (1)	9913 (5)
C(36)′	7214 (5)	6036 (1)	10279 (5)
C(37)′	8351 (4)	5703 (2)	10617 (6)
C(38)′	8280 (3)	5089 (1)	10625 (5)

non-hydrogen atoms in (I)–(III) were refined anisotropically. With the exception of the methanol protons, the positions of all H atoms in (I)–(III) could be located in difference syntheses, and were included in the final cycles. The protons in (II) and (III) were refined with group isotropic temperature factors, those in (I) with individual isotropic temperature factors. Weights were given by the expression $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$; k was fixed at 1·0 for (I), g at respectively 0·0001, 0·0002 and 0·0002 for (I)–(III). An empirical isotropic extinction factor e, defined by $F_c' = F_c(1 - eF_c^2/\sin\theta)$, where F_c' is the modified calculated structure factor, was refined to $0{\cdot}642 \times 10^{-4}$ for (I). Complex neutral-atom scattering factors (Cromer & Waber, 1965; Cromer & Liberman, 1970) were employed for the non-hydrogen atoms. The final atom coordinates are listed in Table 2.* H atom positional parameters and isotropic temperature factors are presented in Table 3, and bond lengths and angles for the non-hydrogen atoms in Tables 4 and 5. Figs. 1–3, which show the molecules (I)–(III) in perspective, were drawn by *RSPLOT* (W. S. Sheldrick), which was also used for the molecular-geometry calculations.

---

* Lists of structure factors and anisotropic thermal parameters for compounds (I)–(III) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35371 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

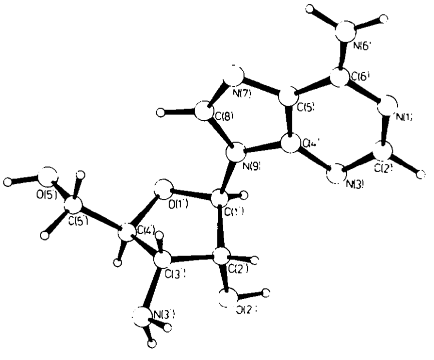

Fig. 1. The molecule of (I) in perspective.

Discussion

The molecular conformation and crystal-packing characteristics of (I)–(III) are summarized in Table 6. All three derivatives adopt an *anti* conformation about the glycosidic C(1′)—N(9) bond. Similar values for χ_{CN} of 19·3, 3·8, 12·4 and 25·7° have been observed in pyromycin (Sundaralingam & Arora, 1969), adenosine 3′-monophosphate dihydrate, adenosine (in a complex with 5-bromouridine) and adenosine 5′-mono-

Table 3. H *atom positional parameters* (×10^4) *with isotropic temperature factors* (Å^2 ×10^3)

	x	*y*	*z*	*U*
Compound (I)				
H(1)	−3312 (25)	−2635 (28)	−5365 (77)	55 (10)
H(61)	404 (23)	−563 (26)	565 (70)	41 (9)
H(62)	−123 (31)	−2144 (24)	1189 (68)	58 (10)
H(8)	−997 (31)	2830 (23)	−6421 (81)	66 (11)
H(1)′	−3002 (24)	1015 (24)	−11230 (49)	29 (7)
H(2)′	−4308 (29)	1476 (31)	−7103 (59)	46 (9)
H(21)′	−5009 (29)	1028 (18)	−11556 (70)	43 (9)
H(3)′	−3409 (25)	3596 (37)	−5934 (46)	48 (9)
H(31)′	−5515 (26)	4062 (42)	−9754 (57)	54 (10)
H(32)′	−5269 (27)	3880 (35)	−6409 (54)	47 (9)
H(4)′	−3785 (20)	4186 (28)	−12134 (42)	26 (7)
H(51)′	−2937 (27)	5940 (25)	−9131 (70)	48 (10)
H(52)′	−1899 (22)	4929 (37)	−7376 (46)	42 (8)
H(53)′	−1753 (29)	6284 (18)	−11656 (75)	50 (9)
Compound (II)				
H(2)	11559 (39)	1619 (23)	6648 (41)	102 (8)
H(61)	13287 (30)	−174 (26)	3928 (55)	102 (8)
H(62)	12233 (37)	−237 (24)	2129 (45)	102 (8)
H(8)	9515 (37)	1195 (25)	−642 (41)	102 (8)
H(1)′	8440 (33)	2167 (21)	3002 (37)	75 (4)
H(2)′	10289 (23)	2909 (21)	2109 (53)	75 (4)
H(21)′	9157 (31)	3788 (19)	3191 (47)	75 (4)
H(3)′	10105 (29)	2780 (20)	−851 (52)	75 (4)
H(4)′	7548 (28)	3153 (19)	−495 (56)	75 (4)
H(51)′	8039 (35)	2938 (17)	−3216 (48)	75 (4)
H(52)′	7203 (23)	2248 (20)	−2576 (59)	75 (4)
H(53)′	9333 (59)	1989 (39)	−3911 (58)	183 (29)
H(31)′	9012 (30)	4144 (19)	−444 (51)	75 (4)
H(32)′	11363 (33)	3718 (20)	−1027 (59)	101 (6)
H(33)′	10063 (27)	5172 (23)	−1382 (69)	101 (6)
H(34)′	11450 (33)	4854 (24)	−2398 (44)	101 (6)
H(35)′	12685 (25)	4884 (27)	−11 (65)	101 (6)
H(36)′	11828 (38)	5552 (16)	564 (59)	101 (6)
H(37)′	11853 (33)	4059 (22)	1624 (60)	101 (6)
H(38)′	10439 (30)	4563 (24)	1771 (57)	101 (6)
Compound (III)				
H(2)	7703 (31)	1441 (13)	16053 (26)	63 (4)
H(61)	8197 (27)	−216 (12)	13311 (34)	63 (4)
H(62)	7388 (33)	−190 (12)	11310 (30)	63 (4)
H(8)	5239 (29)	1525 (13)	8448 (28)	63 (4)
H(1)′	4263 (27)	2320 (14)	12264 (32)	70 (4)
H(2)′	6838 (21)	2777 (14)	11957 (45)	70 (4)
H(3)′	6828 (23)	3118 (14)	8993 (41)	70 (4)
H(4)′	3887 (25)	3291 (12)	8636 (46)	70 (4)
H(51)′	5147 (34)	3152 (11)	16094 (39)	70 (4)
H(52)′	4210 (25)	2446 (11)	16444 (45)	70 (4)
H(53)′	6367 (33)	2293 (14)	15641 (27)	70 (4)
H(31)′	5216 (37)	4231 (12)	12316 (47)	88 (4)
H(32)′	3900 (20)	3780 (15)	11204 (54)	88 (4)
H(33)′	7584 (38)	3945 (15)	11409 (36)	88 (4)
H(34)′	7773 (34)	4001 (17)	9214 (38)	88 (4)
H(35)′	5040 (25)	4912 (15)	9583 (52)	88 (4)
H(36)′	5187 (28)	5977 (15)	9420 (50)	88 (4)
H(37)′	7048 (37)	6496 (8)	10053 (49)	88 (4)
H(38)′	9282 (24)	5940 (14)	10507 (56)	88 (4)
H(39)′	9118 (26)	4817 (14)	10029 (55)	88 (4)

Table 4. *Bond lengths* (Å)

Compound (I)			
C(2)—N(1)	1·340 (3)	C(6)—N(1)	1·354 (3)
N(3)—C(2)	1·332 (3)	C(4)—N(3)	1·350 (3)
C(5)—C(4)	1·387 (3)	N(9)—C(4)	1·367 (3)
C(6)—C(5)	1·406 (3)	N(7)—C(5)	1·384 (3)
N(6)—C(6)	1·336 (3)	C(8)—N(7)	1·311 (3)
N(9)—C(8)	1·368 (3)	C(1)′—N(9)	1·468 (3)
O(1)′—C(1)′	1·405 (3)	C(2)′—C(1)′	1·530 (3)
C(4)′—O(1)′	1·447 (3)	C(3)′—C(2)′	1·526 (3)
O(2)′—C(2)′	1·419 (3)	C(4)′—C(3)′	1·521 (3)
N(3)′—C(3)′	1·465 (3)	C(5)′—C(4)′	1·503 (3)
O(5)′—C(5)′	1·422 (4)		
H(1)—C(2)	1·07 (3)	H(61)—N(6)	1·01 (3)
H(62)—N(6)	1·02 (3)	H(8)—C(8)	1·06 (3)
H(1)′—C(1)′	1·05 (2)	H(2)′—C(2)′	1·07 (3)
H(3)′—C(3)′	1·06 (2)	H(4)′—C(4)′	1·05 (2)
H(21)′—O(2)′	0·98 (2)	H(31)′—N(3)′	0·99 (3)
H(32)′—N(3)′	1·00 (3)	H(51)′—C(5)′	1·06 (3)
H(52)′—C(5)′	1·07 (2)	H(53)′—O(5)′	0·98 (2)
Compound (II)			
C(2)—N(1)	1·330 (5)	C(6)—N(1)	1·366 (5)
N(3)—C(2)	1·318 (5)	C(4)—N(3)	1·361 (5)
C(5)—C(4)	1·367 (5)	N(9)—C(4)	1·375 (5)
C(6)—C(5)	1·399 (5)	N(7)—C(5)	1·405 (5)
N(6)—C(6)	1·333 (5)	C(8)—N(7)	1·305 (5)
N(9)—C(8)	1·365 (5)	C(1)′—N(9)	1·470 (5)
O(1)′—C(1)′	1·420 (5)	C(2)′—C(1)′	1·514 (6)
C(4)′—O(1)′	1·449 (5)	O(2)′—C(2)′	1·400 (5)
C(3)′—C(2)′	1·555 (6)	C(4)′—C(3)′	1·515 (5)
N(3)′—C(3)′	1·446 (5)	C(5)′—C(4)′	1·509 (6)
O(5)′—C(5)′	1·419 (5)	C(31)′—N(3)′	1·454 (5)
C(32)′—C(31)′	1·541 (6)	C(34)′—C(31)′	1·567 (7)
C(33)′—C(32)′	1·539 (8)	C(34)′—C(33)′	1·552 (8)
C—O	1·485 (22)	C′—O′	1·485 (27)
H(2)—C(2)	1·07 (4)	H(71)—N(6)	1·03 (4)
H(72)—N(6)	1·01 (4)	H(8)—C(8)	0·99 (4)
H(1)′—C(1)′	1·07 (3)	H(2)′—C(2)′	1·02 (3)
H(21)′—O(2)′	0·97 (4)	H(3)′—C(3)′	1·05 (4)
H(4)′—C(4)′	1·08 (3)	H(51)′—C(5)′	1·03 (3)
H(52)′—C(5)′	1·10 (3)	H(53)′—O(5)′	1·04 (5)
H(31)′—N(3)′	0·97 (4)	H(32)′—C(31)′	1·07 (4)
H(33)′—C(32)′	1·08 (3)	H(34)′—C(32)′	1·05 (4)
H(35)′—C(33)′	1·09 (3)	H(36)′—C(33)′	1·03 (3)
H(37)′—C(34)′	1·08 (4)	H(38)′—C(34)′	1·08 (4)
Compound (III)			
C(2)—N(1)	1·337 (3)	C(6)—N(1)	1·354 (3)
N(3)—C(2)	1·323 (3)	C(4)—N(3)	1·349 (3)
C(5)—C(4)	1·384 (3)	N(9)—C(4)	1·373 (3)
C(6)—C(5)	1·399 (3)	N(7)—C(5)	1·386 (3)
N(6)—C(6)	1·336 (3)	C(8)—N(7)	1·316 (3)
N(9)—C(8)	1·372 (3)	C(1)′—N(9)	1·483 (3)
O(1)′—C(1)′	1·391 (3)	C(2)′—C(1)′	1·519 (4)
C(4)′—O(1)′	1·450 (3)	O(2)′—C(2)′	1·422 (3)
C(3)′—C(2)′	1·542 (4)	C(31)′—O(2)′	1·443 (3)
C(4)′—C(3)′	1·530 (4)	N(3)′—C(3)′	1·466 (3)
C(5)′—C(4)′	1·514 (4)	O(5)′—C(5)′	1·410 (4)
C(31)′—N(3)′	1·444 (4)	C(32)′—N(3)′	1·465 (4)
C(33)′—C(32)′	1·509 (4)	C(34)′—C(33)′	1·374 (4)

Table 4 (*cont.*)

C(38)′–C(33)′	1·375 (4)	C(35)′–C(34)′	1·386 (4)
C(36)′–C(35)′	1·378 (5)	C(37)′–C(36)′	1·377 (6)
C(38′–C(37)′	1·378 (5)		
H(2)–C(2)	1·07 (2)	H(61)–N(6)	1·00 (3)
H(62)–N(6)	0·98 (3)	H(8)–C(8)	1·05 (2)
H(1)′–C(1)′	1·06 (3)	H(2)′–C(2)′	1·07 (2)
H(3)′–C(3)′	1·06 (3)	H(4)′–C(4)′	1·08 (3)
H(51)′–C(5)′	1·05 (3)	H(52)′–C(5)′	1·08 (3)
H(53)′–O(5)′	0·98 (2)	H(31)′–C(31)′	1·06 (3)
H(32)′–C(31)′	1·11 (2)	H(33)′–C(32)′	1·07 (3)
H(34)′–C(32)′	1·08 (3)	H(35)′–C(34)′	1·07 (3)
H(36)′–C(35)′	1·05 (3)	H(37)′–C(36)′	1·06 (2)
H(38)′–C(37)′	1·07 (3)	H(39)′–C(38)′	1·06 (3)

Table 5. *Bond angles* (°)

Compound (I)			
C(6)–N(1)–C(2)	119·8 (2)	N(3)–C(2)–N(1)	128·5 (2)
C(4)–N(3)–C(2)	110·5 (2)	C(5)–C(4)–N(3)	127·4 (2)
N(9)–C(4)–N(3)	126·7 (2)	N(9)–C(4)–C(5)	106·0 (2)
C(6)–C(5)–C(4)	116·7 (2)	N(7)–C(5)–C(4)	110·3 (2)
N(7)–C(5)–C(6)	133·0 (2)	C(5)–C(6)–N(1)	117·2 (2)
N(6)–C(6)–N(1)	118·5 (2)	N(6)–C(6)–C(5)	124·4 (2)
C(8)–N(7)–C(5)	104·0 (2)	N(9)–C(8)–N(7)	113·7 (2)
C(8)–N(9)–C(4)	106·0 (2)	C(1)′–N(9)–C(4)	124·5 (2)
C(1)′–N(9)–C(8)	129·5 (2)	O(1)′–C(1)′–N(9)	109·5 (2)
C(2)′–C(1)′–N(9)	111·7 (2)	C(2)′–C(1)′–O(1)′	107·0 (2)
C(4)′–O(1)′–C(1)′	110·3 (2)	C(3)′–C(2)′–C(1)′	101·1 (2)
O(2)′–C(2)′–C(1)′	109·0 (2)	O(2)′–C(2)′–C(3)′	108·5 (2)
C(4)′–C(3)′–C(2)′	102·1 (2)	N(3)′–C(3)′–C(2)′	116·1 (2)
N(3)′–C(3)′–C(4)′	112·5 (2)	C(3)′–C(4)′–O(1)′	105·0 (2)
C(5)′–C(4)′–O(1)′	108·7 (2)	C(5)′–C(4)′–C(3)′	116·5 (2)
O(5)′–C(5)′–C(4)′	108·8 (2)		
Compound (II)			
C(6)–N(1)–C(2)	118·9 (3)	N(3)–C(2)–N(1)	129·6 (4)
C(4)–N(3)–C(2)	110·2 (3)	C(5)–C(4)–N(3)	126·9 (3)
N(9)–C(4)–N(3)	126·5 (3)	N(9)–C(4)–C(5)	106·7 (3)
C(6)–C(5)–C(4)	117·7 (3)	N(7)–C(5)–C(4)	110·2 (3)
N(7)–C(5)–C(6)	132·2 (3)	C(5)–C(6)–N(1)	116·7 (3)
N(6)–C(6)–N(1)	117·5 (3)	N(6)–C(6)–C(5)	125·8 (3)
C(8)–N(7)–C(5)	103·4 (3)	N(9)–C(8)–N(7)	114·4 (3)
C(8)–N(9)–C(4)	105·3 (3)	C(1)′–N(9)–C(4)	124·3 (3)
C(1)′–N(9)–C(8)	130·3 (3)	O(1)′ C(1)′ N(9)	108·8 (3)
C(2)′–C(1)′–N(9)	112·7 (3)	C(2)′–C(1)′–O(1)′	107·5 (3)
C(4)′–O(1)′–C(1)′	109·4 (3)	O(2)′–C(2)′–C(1)′	109·7 (3)
C(3)′–C(2)′–C(1)′	100·8 (3)	C(3)′–C(2)′–O(2)′	107·3 (3)
C(4)′–C(3)′–C(2)′	101·0 (3)	N(3)′–C(3)′–C(2)′	117·8 (3)
N(3)′–C(3)′–C(4)′	112·3 (3)	C(3)′–C(4)′–O(1)′	105·6 (3)
C(5)′–C(4)′–O(1)′	109·2 (3)	C(5)′–C(4)′–C(3)′	116·3 (3)
O(5)′–C(5)′–C(4)′	109·8 (3)	C(31)′–N(3)′–C(3)′	116·2 (3)
C(32)′–C(31)′–N(3)′	116·3 (4)	C(34)′–C(31)′–N(3)′	122·5 (4)
C(34)′–C(31)′–C(32)′	88·0 (4)	C(33)′–C(32)′–C(31)′	88·3 (4)
C(34)′–C(33)′–C(32)′	88·7 (4)	C(33)′–C(34)′–C(31)′	86·9 (4)
Compound (III)			
C(6)–N(1)–C(2)	118·4 (2)	N(3)–C(2)–N(1)	129·3 (3)
C(4)–N(3)–C(2)	111·0 (2)	C(5)–C(4)–N(3)	126·1 (2)
N(9)–C(4)–N(3)	127·9 (2)	N(9)–C(4)–C(5)	106·1 (2)
C(6)–C(5)–C(4)	117·4 (2)	N(7)–C(5)–C(4)	110·3 (2)
N(7)–C(5)–C(6)	132·2 (2)	C(5)–C(6)–N(1)	117·6 (2)
N(6)–C(6)–N(1)	117·9 (2)	N(6)–C(6)–C(5)	124·5 (2)
C(8)–N(7)–C(5)	104·3 (2)	N(9)–C(8)–N(7)	113·3 (2)
C(8)–N(9)–C(4)	106·0 (2)	C(1)′–N(9)–C(4)	125·7 (2)
C(1)′–N(9)–C(8)	127·6 (2)	O(1)′–C(1)′–N(9)	108·1 (2)
C(2)′–C(1)′–N(9)	111·8 (2)	C(2)′–C(1)′–O(1)′	108·7 (2)
C(4)′–O(1)–C(1)′	111·8 (2)	O(2)′–C(2)′–C(1)′	110·7 (2)
C(3)′–C(2)′–Ç(1)′	104·8 (2)	C(3)′–C(2)′–O(2)′	104·7 (2)
C(31)′–O(2)′–C(2)′	108·2 (2)	C(4)′–C(3)′–C(2)′	104·5 (2)
N(3)′–C(3)′–C(2)′	105·2 (2)	N(3)′–C(3)′–C(4)′	112·1 (2)
C(3)′–C(4)′–O(1)′	107·2 (2)	C(5)′–C(4)′–O(1)′	109·9 (2)
C(5)′–C(4)′–C(3)′	114·8 (2)	O(5)′–C(5)′–C(4)′	108·8 (2)
C(31)′–N(3)′–C(3)′	102·5 (2)	C(32)′–N(3)′–C(3)′	111·6 (2)
C(32)′–N(3)′–C(31)′	113·9 (2)	N(3)′–C(31)′–O(2)′	107·7 (2)
C(33)′–C(32)′–N(3)′	114·4 (2)	C(34)′–C(33)′–C(32)′	123·7 (3)
C(38)′–C(33)′–C(32)′	117·7 (3)	C(38)′–C(33)′–C(34)′	118·6 (3)
C(35)′–C(34)′–C(33)′	120·6 (3)	C(36)′–C(35)′–C(34)′	120·3 (3)
C(37)′–C(36)′–C(35)′	119·2 (3)	C(38)′–C(37)′–C(36)′	120·0 (3)
C(37)′–C(38)′–C(33)′	121·3 (3)		

Table 6. *Molecular conformation and crystal-packing characteristics*

	(I)	(II)	(III)
Glycosidic torsion angle	*anti*	*anti*	*anti*
χ_{CN} [O(1′)–C(1′)–N(9)–C(8)]	10·0 (2)°	16·5 (3)°	−1·3 (2)°
Conformation of C(5′)–O(5′)	*gauche–trans*	*gauche–gauche*	*gauche–gauche*
ψ_{OO} [O(5′)–C(5′)–C(4′)–O(1′)]	57·4 (2)	−59·4 (3)	−74·5 (2)
ψ_{OC}[O(5′)–C(5′)–C(4′)–C(3′)]	175·7 (2)	59·8 (3)	46·4 (2)
Ribose conformation	C(3′)-*endo*	C(3′)-*endo*	C(2′)-*exo*
Base-stacking type	Translation	No stacking	No stacking
Distance between base planes (Å)	3·53	—	—
Degree of base overlap	0·0%	—	—

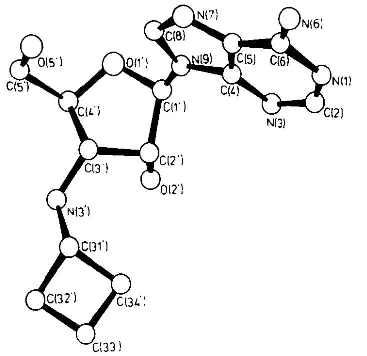

Fig. 2. The molecule of (II) in perspective.

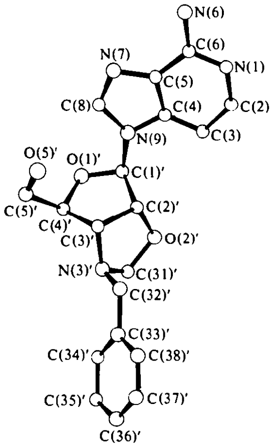

Fig. 3. The molecule of (III) in perspective.

phosphate monohydrate (Sundaralingam, 1969). Computed steric barriers to rotation about the glycosidic bond have indicated that the mode of sugar puckering will determine the possible values of χ_{CN} (Haschemeyer & Rich, 1967). In purine nucleosides and nucleotides with C(3′)-*endo* puckering, as observed for (I) and (II) and the above-mentioned derivatives, only the *anti* conformation in the range −150 to +20° should be preferred. In (I) and (II), C(3′) is displaced by respectively 0·566 and 0·598 Å on the same side as C(5′) from the least-squares plane through the remaining four ribose ring atoms.

Table 7. *Hydrogen bonding in* (I)–(III) [*presented as observed hydrogen bond, symmetry position of the second nonhydrogen atom with respect to the first atom, and bond distance* (Å)]

N(6)–H(61)···O(5′) −*x*, 0·5 + *y*, −*z* 2·89 (1)	N(1)···H(62)–N(6) 0·5 − *x*, −*y*, 0·5 + *z* 2·94 (1)	N(1)···H(62)–N(6) 0·5 − *x*, −*y*, 0·5 + *z* 2·95 (1)
O(2′)–H(21′)···N(3′) −*x*, 0·5 + *y*, −*z* 2·81 (1)	N(3)···H(53′)–O(5′) *x*, *y*, 1·0 + *z* 2·82 (1)	N(3)···H(53′)–O(5′) *x*, *y*, 1·0 + *z* 2·80 (1)
	N(6)–H(61)···N(7) 0·5 − *x*, −*y*, 0·5 + *z* 3·05 (1)	N(6)–H(61)···N(7) 0·5 − *x*, −*y*, 0·5 + *z* 3·04 (1)
	O(2′)–H(21′)···O 2,*y*,*z* 2·80 (1)	
	O(2′)=H(21)′···O′ *x*,*y*,*z* 2·80 (1)	

With the nomenclature of Sundaralingam (1975), the conformation of the ribose ring in (I) and (II) may also be described as twist $^3T_2$. C(2′) and C(3′) are displaced by respectively 0·260 and 0·358 Å in (I) and 0·244 and 0·405 Å in (II) on opposite sides of the plane C(1′)O(1′)C(4′). As a result of the oxazolidine ring formation in (III), the ribose ring is markedly less puckered, its conformation being the unusual C(2′)-*exo*, with C(2′) displaced, however, only 0·272 Å from the least-squares plane of the remaining four ring atoms. Other distances from this plane are C(1′) 0·008, C(2′) −0·013, C(3′) −0·007 and C(4′) 0·012 Å.

Whereas the position of the C(5′)–O(5′) bond relative to the ribose ring is *gauche–gauche* in (II) and (III), a *gauche–trans* conformation is observed in (I). O(5′) participates in intermolecular O···H–N hydrogen bonding to N(6) in (I) but in O–H···N intermolecular hydrogen bonding to N(3) in (II) and (III), Table 7. As a result of the small value of $\chi_{\rm CN}$ and the *gauche–gauche* position of C(5′)–O(5′), short O(5′)···C(8) intramolecular distances are observed in (II) and (III). The O(5′)···C(8) distances are 3·16 and 3·22 Å with respective O(5′)···H(8) distances of 2·28 and 2·54 Å. In contrast to the N(6) protons, the N(3′) protons in (I) and (II) do not participate in hydrogen bonding. N(3′) is intermolecularly hydrogen bonded to O(2′) in (I). With the exception of the O(2′)–H(21′)···O and O(2′)–H(21′)···O′ bonds to the disordered methanol O atoms in (II), the pattern of hydrogen bonding in (II) and (III) is identical. In both these derivatives no adenine base stacking is observed. Parallel adenine bases in (I) are related to one another at a distance of 3·53 Å by translation along **c**. There is no overlap of neighboring adenine systems. This mode of stacking (pattern I, Motherwell & Isaacs, 1972) is typical of purine nucleosides and nucleotides in the *anti* configuration with $\chi_{\rm CN} \approx 10 \pm 20°$ (Schomburg, 1978). As a result of potential steric interaction between neighboring sugar rings no base overlap is to be expected for this stacking mode. The absence of base stacking in (II) and (III) for which the translation mode would also be expected is presumably a result of the bulkiness of the 3′-substituents, which prevents an adequate proximity of the adenine π systems in this mode.

References

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Gerber, N. N. & Lechevalier, H. A. (1962). *J. Org. Chem.* **27**, 1731–1732.

Haschemeyer, A. E. V. & Rich, A. (1967). *J. Mol. Biol.* **27**, 369–384.

Morr, M. & Ernst, L. (1979). *Chem. Ber.* **112**, 2815–2828.

Motherwell, W. D. S. & Isaacs, N. W. (1972). *J. Mol. Biol.* **71**, 231–241.

Schomburg, I. (1978). Diplomarbeit, Tech. Univ. Braunschweig, pp. 36–39.

Sundaralingam, M. (1969). *Biopolymers*, **7**, 821–860.

Sundaralingam, M. (1975). *Ann. N.Y. Acad. Sci.* **225**, 3–42.

Sundaralingam, M. & Arora, S. K. (1969). *Proc. Natl Acad. Sci. U.S.A.* **64**, 1021–1026.

Acta Cryst. (1980). B**36**, 2333–2337

Structure of t-2,c-4,t-6-Trimethyl-1λ^4,3,5-trithiane r-1-Oxide

By Mami Mikami-Kido, Michiko Konno and Yoshihiko Saito

The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, *Japan*

(*Received* 4 *June* 1979; *accepted* 29 *April* 1980)

Abstract

The crystal structure of the title compound, $C_6H_{12}OS_3$, was determined by X-ray diffraction. The space group is *Pbca* with a = 11·763 (2), b = 19·102 (2), c = 8·261 (1) Å and Z = 8. The structure was refined to R = 0·037 for 1834 reflections collected by diffractometry. The 1,3,5-trithiane ring takes a chair

0567-7408/80/102333-05$01.00