by the torsion angle 174·2 (4)° for the atom sequence C(12)–O(4)–C(1)–C(9).

The extensive system of hydrogen bonds in the crystal structure of (1) is illustrated in Fig. 2.* There are no intramolecular hydrogen bonds and neither the glycosidic bridge O nor the ring O atoms are hydrogen-bonded. Two hydroxyl groups in the molecule exhibit both donor and acceptor functions. Each molecule is linked to a neighbour by O(5)–H(5*A*)···O(8); C(1)–H(1)···O(3)($-1+x, y, z$) to form chains parallel to **a**. The water molecule is involved in three hydrogen bonds [O(1)–H(1*B*)···O(6)($x, y, 1+z$), O(1)–H(1*A*)···O(7) ($1+x, y, 1+z$) and O(7)–H(7)···O(1)($1-x, -0·5+y, 1-z$)] with three neighbouring molecules.

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* See deposition footnote.

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Acta Cryst. (1986). C**42**, 1027–1029

cis-Thymidine 3′,5′-Cyclic Methylphosphonate Acetone Solvate, a Cyclic Nucleotide with an Axial Methyl Group on Phosphorus

By Wesley G. Bentrude,* Alan E. Sopchik, Gurdip S. Bajwa and William N. Setzer

Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112, *USA*

and William S. Sheldrick*†

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

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Abstract. $C_{11}H_{15}N_2O_6P.C_3H_6O$, $M_r = 360·30$, monoclinic, $C2$, $a = 18·298$ (6), $b = 7·251$ (2), $c = 13·618$ (2) Å, $\beta = 96·41$ (3)°, $V = 1795·5$ Å^3, $Z = 4$, $D_x = 1·33$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 16·82$ cm^{-1}, $F(000) = 760$, $T = 293$ K, $R = 0·039$ for 1622 unique observed reflections. The compound crystallizes with one cyclic nucleotide molecule and one acetone solvent molecule in the asymmetric unit. The conformation of the thymine base is *anti*. The ribose ring adopts a T_4^3 [C(4′)-*exo*/C(3)′-*endo*] (half-chair) conformation, and the phosphonate ring adopts a flattened-chair conformation with the methyl group axial.

Introduction. We have been interested in the conformational consequences of phosphorus substituents in 3′,5′-cyclic nucleotides. Recently we have studied, using NMR (Nelson, Sopchik & Bentrude, 1983; Bajwa & Bentrude, 1978, 1980; Sopchik, Bajwa, Nelson & Bentrude, 1981; Sopchik & Bentrude, 1980) and X-ray diffraction (Bentrude, Sopchik, Setzer, Bates & Ortega, 1986; Newton, Pantaleo, Bajwa & Bentrude, 1977), the conformational properties of neutral derivatives of nucleoside 3′,5′-cyclic monophosphates. This paper reports the crystal structure of *cis*-thymidine 3′,5′-cyclic methylphosphonate, (1), a cyclic nucleotide

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* Address correspondence to these authors.

† Current address: Universität Kaiserslautern, Postfach 3049, D-6750 Kaiserslautern, Federal Republic of Germany.

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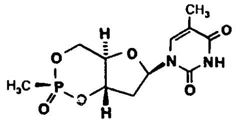
with an axially disposed methyl substituent on the P atom of the 1,3,2-dioxaphosphorinane ring.



(1)

Experimental. *Preparation of thymidine 3′,5′-cyclic methylphosphonate.* Methyl iodide (6·0 mL, 13·7 g, 94·5 mmol) and methyl thymidine 3′,5′-cyclic phosphite (1·2 g, 3·97 mmol) (Bajwa & Bentrude, 1978) were combined and stirred at room temperature for four days. The excess methyl iodide was removed *in vacuo* and the residue chromatographed by MPLC on a 15 × 1000 mm column of silica gel (Merck, 230–400 mesh), eluting with EtOAc/EtOH (85:15), to give 509 mg of pure *trans*-phosphonate: ^{31}P NMR (CDCl$_3$) δ 33·1, and 320 mg of pure *cis*-phosphonate: ^{31}P NMR (CDCl$_3$) δ 27·5 (Bajwa & Bentrude, 1980).

X-ray structure determination. Colorless prism, 0·48 × 0·56 × 0·24 mm; Syntex $P2_1$ diffractometer, cell parameters refined by least-squares method from setting angles of 15 reflections in range $30 \leq 2\theta \leq 40°$; intensities collected with Cu $K\alpha$ radiation, $3 \leq 2\theta \leq 130°$, θ–2θ scan; h −21 to 21, k 0 to 8, l 0 to 16; standard reflections 510, 040, 115 with intensity variations < ±0·8%; intensities corrected empirically for absorption, ψ scan with intervals of 20° for 20 strong reflections, min./max. transmission factors 0·243/0·422, data reduced to F_o and $\sigma(F_o)$, data with $F_o^2 \geq 1{\cdot}5\sigma(F_o^2)$ considered observed (1622 of 1670 unique data), $R_{\rm int} = 0{\cdot}018$; structure solved by heavy-atom method, atoms located by difference maps; structure refined (PDP 20 computer) by full-matrix least squares (*SHELX76*, Sheldrick, 1976), H atoms calculated geometrically; methyl protons of C(7′) and of acetone refined as rigid groups with d(C—H) = 1·08 Å and tetrahedral bond angles; group isotropic temperature factors for acetone protons, remaining H atoms assigned individual isotropic temperature factors and allowed to ride on corresponding C or N atoms with d(C—H) = 1·08 Å and d(C—N) = 0·99 Å; correction for isotropic secondary extinction included in refinement, $g = 0{\cdot}38\,(4) \times 10^{-6}$; final conventional $R = 0{\cdot}039$, $wR = 0{\cdot}043$, $w = 5{\cdot}4178[\sigma^2(F_o) + 0{\cdot}0002F_o^2]^{-1}$; largest peak in final difference map 0·21 e Å^{-3}; ratio of max. LS shift to e.s.d. 0·19; atomic scattering factors from *SHELX76*.

Discussion. The final atomic parameters for (1) are listed in Table 1.* A perspective view of the molecule† along with the labeling scheme is given in Fig. 1. Bond lengths and selected bond angles are shown in Fig. 2.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters for* (1)

$U_{\rm eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	y	z	$U_{\rm eq}$(Å^2)
P	0·8636 (1)*	1·0000	0·9651 (1)	54 (1)
N(1)	0·6710 (1)	0·7123 (4)	0·6311 (2)	47 (1)
C(2)	0·6027 (1)	0·7071 (5)	0·5774 (2)	51 (1)
O(2)	0·5455 (1)	0·7067 (5)	0·6156 (1)	69 (1)
N(3)	0·6035 (1)	0·7027 (5)	0·4764 (2)	58 (1)
C(4)	0·6650 (2)	0·7064 (6)	0·4246 (2)	58 (2)
O(4)	0·6575 (1)	0·7001 (6)	0·3351 (1)	89 (2)
C(5)	0·7346 (2)	0·7207 (5)	0·4863 (2)	49 (1)
C(6)	0·7343 (2)	0·7255 (5)	0·5843 (2)	47 (1)
C(7)	0·8038 (2)	0·7286 (6)	0·4366 (2)	60 (2)
C(1′)	0·6730 (2)	0·7218 (5)	0·7389 (2)	45 (1)
O(4′)	0·6680 (1)	0·9147 (3)	0·7635 (1)	52 (1)
C(2′)	0·7445 (2)	0·6472 (5)	0·7970 (2)	49 (1)
C(3′)	0·7822 (1)	0·8245 (5)	0·8312 (2)	44 (1)
O(3′)	0·8329 (1)	0·8094 (4)	0·9197 (1)	51 (1)
C(4′)	0·7181 (1)	0·9448 (5)	0·8502 (2)	44 (1)
C(5′)	0·7412 (2)	1·1408 (5)	0·8649 (2)	56 (2)
O(5′)	0·7966 (1)	1·1388 (4)	0·9506 (2)	63 (1)
O(6′)	0·8907 (1)	0·9790 (5)	1·0697 (1)	71 (1)
C(7′)	0·9294 (2)	1·0812 (7)	0·8899 (2)	69 (2)
C(11)	0·4654 (2)	0·1704 (8)	0·7151 (3)	89 (3)
O(11)	0·4041 (2)	0·2074 (11)	0·6815 (3)	149 (4)
C(12)	0·5290 (4)	0·2439 (17)	0·6794 (8)	190 (8)
C(13)	0·4821 (5)	0·0596 (15)	0·8057 (6)	154 (6)

* E.s.d.'s are in parentheses.

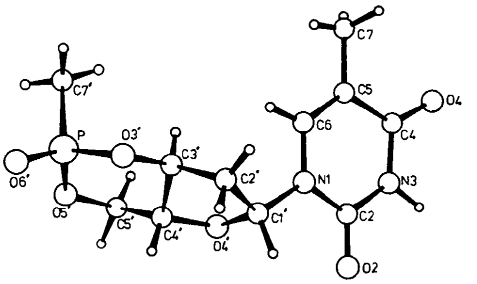


Fig. 1. Perspective view of *cis*-thymidine 3′,5′-cyclic methylphosphonate, (1).

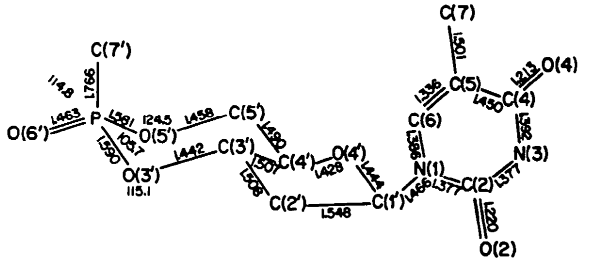


Fig. 2. Bond lengths (Å) and selected bond angles (°) in *cis*-thymidine 3′,5′-cyclic methylphosphonate, (1). (Average e.s.d.'s 0·004 Å and 0·3°.)

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond lengths, bond angles, and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42764 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Fig. 1 was drawn using *RSPLOT*, written by W. S. Sheldrick.

The compound crystallizes with one nucleotide molecule and one acetone solvent molecule in the asymmetric unit. There are no particularly short contacts between the acetone and nucleotide molecules. The nucleotide molecules are linked *via* O(2)···H(3)—N(3) intermolecular hydrogen bonds of length 2·871 (4) Å [O(2)···H(3) = 1·93 (1) Å] into dimers with crystallographic twofold symmetry.

The thymine base in (1) adopts, in the crystal, the *anti* conformation. The torsion angle about the glycosidic bond, χ, O(4′)—C(1′)—N(1)—C(2), is 267·8°.* Both *syn* and *anti* conformations have been found in neutral derivatives of pyrimidine cyclic nucleotides (Bentrude *et al.*, 1986, and references therein). For example, in *cis*-thymidine 3′,5′-cyclic *N*,*N*-dimethylphosphoramidate, (2) [C(7′)CH_3 of (1) equals $(CH_3)_2N$], the base is also *anti* (χ = 252·8 and 233·1°) (Bentrude *et al.*, 1986). In the *trans*-phosphoramidate, however, the *syn* conformation (χ = 82·6°) has been found in the crystal (Newton *et al.*, 1977).

The ribose of (1) is seen to adopt the T_4^3 (half-chair) conformation (Sundaralingam & Abola, 1972). The C(4′)—O(4′)—C(1′)—C(2′), ν_0, and O(4′)—C(1′)—C(2′)—C(3′), ν_1, torsion angles are −16·0 and −13·0°, respectively. Interestingly, in the *cis*-phosphoramidate, (2) (Bentrude *et al.*, 1986), the ribose ring adopts a ${}_4E$ (envelope) conformation where ν_0 and ν_1 average −28·3 and 1·5°, respectively. The *trans*-phosphoramidate (Newton *et al.*, 1977) shows the ribose ring to be in a ${}_4T^3$ (twist-envelope) conformation ($\nu_0 = -23{\cdot}0$, $\nu_1 = -5{\cdot}5°$).

The O(3′)—P—O(5′)—C(5′) and O(5′)—P—O(3′)—C(3′) torsion angles of −36·5 and 38·2°, respectively, indicate the phosphorus end of the chair-form 1,3,2-dioxaphosphorinane ring to be flattened. Such ring flattening has been observed in the *cis*-phosphoramidate, (2), [O(3′)—P—O(5′)—C(5′) and O(5′)—P—O(3′)—C(3′) average −37·9 and 39·5°, respectively] (Bentrude *et al.*, 1986), in the *trans*-phosphoramidate [O(3′)—P—O(5′)—C(5′) = −44·3, O(5′)—P—O(3′)—C(3′) = 48·3°] (Newton *et al.*, 1977), and in 1,3,2-dioxaphosphorinanes in general (Warrent, Caughlan, Hargis, Yee & Bentrude, 1978).

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* The atom labeling and definitions of χ, ν_0 and ν_1 are according to *Eur. J. Biochem.* (1983), **131**, 9–15.

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Structure of Pivaloyloxymethyl (3*S*,5*R*)-6,6-Dibromopenicillanate 1,1-Dioxide

By Pedro M. Alzari,* Blas E. Rivero, Graciela Punte and Alicia E. Ronco

Laboratorio de Cristalografía, Departamento de Fisica, Universidad Nacional de La Plata, CC 67,
1900 *La Plata, Argentina*

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Abstract. $C_{14}H_{19}Br_2NO_7S$, $M_r = 505{\cdot}2$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}241$ (1), $b = 10{\cdot}478$ (1), $c = 20{\cdot}082$ (3) Å, $V = 1944{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}726$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 62{\cdot}4$ cm^{-1}, $F(000) = 1008$, room temperature, final $R = 0{\cdot}040$ for 1348 independent reflections. The thiazolidine ring adopts a conformation with the sulfur atom 0·80 (1) Å

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* Present address: Immunologie Structurale, Institut Pasteur, 25 Rue du Dr Roux, 75724 Paris CEDEX 15, France.

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