Table 9. *Selected geometry (Å, °) for phosphoglycolate moieties*

	(I)	(IIA)	(IIB)	(IIIA)	(IIIB)	(IV)
P—O1	1.508 (2)	1.506 (2)	1.493 (2)	1.562 (1)	1.552 (1)	1.518 (2)
P—O2	1.596 (2)	1.594 (2)	1.580 (2)	1.600 (1)	1.599 (1)	1.625 (2)
P—O3	1.496 (2)	1.501 (2)	1.502 (2)	1.506 (1)	1.514 (1)	1.507 (2)
P—O4	1.563 (2)	1.558 (2)	1.577 (2)	1.504 (1)	1.498 (1)	1.521 (2)
O2—C2	1.425 (2)	1.420 (2)	1.422 (2)	1.430 (2)	1.421 (2)	1.426 (2)
O5—C1	1.212 (2)	1.207 (3)	1.227 (3)	1.242 (2)	1.244 (2)	1.252 (2)
O6—C1	1.309 (2)	1.309 (2)	1.285 (2)	1.267 (2)	1.267 (2)	1.259 (2)
C1—C2	1.510 (2)	1.493 (3)	1.516 (3)	1.513 (2)	1.513 (2)	1.517 (2)
O1—P—O2	103.9 (1)	104.7 (1)	105.1 (1)	99.7 (1)	98.8 (1)	103.3 (1)
O1—P—O3	115.6 (1)	116.1 (1)	117.8 (1)	111.6 (1)	112.2 (1)	112.9 (1)
O1—P—O4	109.4 (1)	108.4 (1)	111.4 (1)	111.8 (1)	113.0 (1)	113.0 (1)
O2—P—O3	110.7 (1)	109.9 (1)	110.2 (1)	110.1 (1)	109.1 (1)	107.4 (1)
O2—P—O4	105.2 (1)	106.2 (1)	106.4 (1)	108.9 (1)	110.7 (1)	106.9 (1)
O3—P—O4	111.3 (1)	110.9 (1)	105.5 (1)	113.9 (1)	112.2 (1)	112.6 (1)
C2—O2—P	120.1 (2)	121.1 (2)	124.6 (2)	117.9 (1)	118.7 (1)	116.4 (2)
O2—C2—C1	112.8 (2)	113.1 (2)	108.6 (2)	110.3 (1)	110.4 (1)	110.8 (2)
O5—C1—O6	124.7 (2)	124.5 (3)	124.8 (2)	126.2 (1)	126.6 (1)	125.1 (2)
O5—C1—C2	124.7 (2)	123.9 (3)	120.1 (2)	120.4 (1)	120.2 (1)	119.5 (2)
O6—C1—C2	110.5 (2)	111.3 (2)	115.2 (2)	113.3 (1)	113.1 (1)	115.4 (2)
O1—P—O2—C2	−164.4 (1)	−162.8 (2)	−161.6 (2)	−166.5 (1)	−178.9 (1)	176.5 (2)
O3—P—O2—C2	70.9 (2)	71.8 (2)	−33.8 (2)	76.1 (1)	63.8 (1)	57.0 (2)
O4—P—O2—C2	−49.4 (2)	−48.2 (2)	80.2 (2)	−49.4 (1)	−60.1 (1)	−64.1 (2)
P—O2—C2—C1	−93.4 (2)	−109.0 (2)	153.4 (2)	171.3 (1)	172.5 (1)	179.5 (2)
O5—C1—C2—O2	−6.0 (2)	−1.1 (8)	−7.9 (3)	−11.8 (2)	−1.9 (2)	1.6 (3)
O6—C1—C2—O2	174.9 (2)	−175.1 (2)	172.5 (2)	170.2 (1)	177.8 (1)	−178.6 (2)

The collection of data at low temperature was carried out using an Oxford Cryosystem cooler for all compounds. In the case of (II), an additional peak near O5*A* was found on a difference map. It was interpreted in terms of the disordering of this atom over the sites O5*A* and O51*A*.

For all compounds, data collection: *KM4 Software* (Kumar Diffraction, 1989); cell refinement: *KM4 Software*; data reduction: *KM4 Software*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1249). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-Amino-1-(2-deoxy-β-D-ribofuranosyl)-6,7-dihydro-1*H*,5*H*-cyclopentapyrimidine-2-one

STEPHEN NEIDLE,[a] DANIEL C. CAPALDI,[b] COLIN B. REESE[b] AND PETER D. ROSELT[b]

[a]*CRC Biomolecular Structure Unit, The Institute of Cancer Research, Cotswold Road, Sutton, Surrey SM2 5NG, England, and* [b]*Department of Chemistry, King's College London, Strand, London WC2R 2LS, England. E-mail: steve@iris5.icr.ac.uk*

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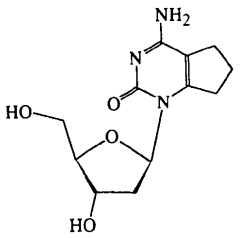
Abstract

The crystal structure of $C_{12}H_{17}N_3O_4$ has been determined. This modified base is in a *syn* conformation with respect to the deoxyribose sugar, which adopts a distorted C3′/O4′-*endo* pucker.

Comment

The crystal structure of this modified nucleoside, (I), was determined as part of a project to assess the effect of the bulky cyclopentene ring on the conformation of cytosine itself, and ultimately on DNA structures when incorporated into an oligonucleotide. Results from these studies will be reported elsewhere. This is the first reported crystal structure of a cytosine derivative with a cyclic aliphatic group attached at the 5 and 6 positions.



(I)

The molecule adopts a *syn* conformation about the glycosidic bond, with a value of 64.4 (3)° for the glycosidic angle (O4′—C1′—N1—C2). This is unusual for pyrimidines, which are normally observed in the *anti* conformation (Neidle, 1994). Molecular-mechanics energy calculations using the *HYPERCHEM* program (Hypercube Inc., 1994) indicate that the crystallographic *syn* conformation and the *anti* conformation, produced by a rotation of 180° about the glycosidic angle, differ by 1.7 kcal mole^{-1} (1 kcal = 4.184 kJ), with the former having the lower energy. The *anti* conformation results in close contacts between the H atoms on C7 and C2′/C3′ of the furanose ring. This could be relieved by sugar repuckering, which occurred on molecular-mechanics minimizations of the two conformations, *syn* and *anti*. The difference in energies for the two conformers was then only 0.2 kcal mole^{-1}, albeit still in favour of the *syn* conformation. Equivalent calculations on cytosine itself show the *anti* conformation to be favoured by 1.3 kcal mole^{-1}, suggesting that the cyclopentenyl derivation has resulted in a slight shift towards a *syn* conformational preference.

The deoxyribose sugar has a distorted pucker intermediate between C3′-*endo* and O4′-*endo*, with a pseudorotation phase angle, *P*, of 56.2° and a maximum degree of pucker of 39.9°. The exocyclic torsion angle O5′—C5′—C4′—C3′, with a value of 53.6 (4)°, is in the common *gauche*$^+$ domain.

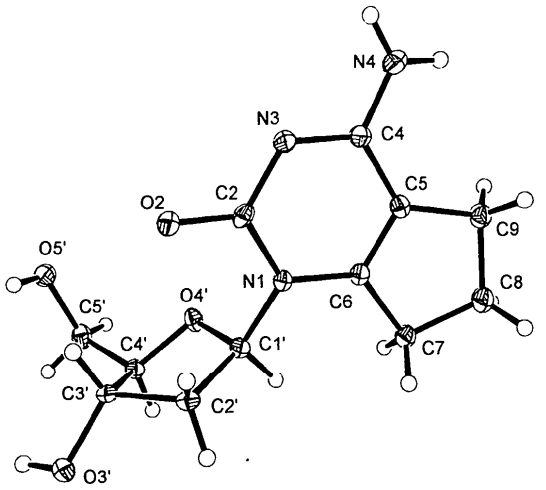


Fig. 1. A view of the title structure. Displacement ellipsoids are shown at the 50% probability level. H atoms have been drawn as small circles of arbitrary radius.

Bond lengths and angles for the cytosine base agree closely with standard values (Clowney *et al.*, 1996; Gelbin *et al.*, 1996), as do most of the values for the sugar ring and its substituents. A few, such as the C1′—C2′ distance, differ by several e.s.d.'s. This may be a consequence of the well established dependence of nucleoside sugar geometry on pucker type.

The cytosine base is significantly non-planar with the substituent atom N4 deviating by 0.093 (2) Å from the least-squares plane defined by N1,C2,O2,N3,C4,N4,-C5,C6, and an r.m.s. deviation for the six non-H ring atoms and two substituent atoms of 0.066 Å. The cyclopentene ring is closely coplanar, with a r.m.s. deviation of 0.020 Å and no ring atom deviating by more than 0.028 (2) Å from the least-squares plane. The dihedral angle between this plane and that of the cytosine ring is 8.0 (1)°.

Experimental

The title compound was crystallized by slow evaporation from ethanolic solution. Details of the synthesis will be published elsewhere.

Crystal data

$C_{12}H_{17}N_3O_4$
M_r = 267.29
Orthorhombic
$P2_12_12_1$
a = 9.543 (4) Å
b = 10.2790 (10) Å
c = 12.231 (5) Å
V = 1199.8 (7) Å^3
Z = 4
D_x = 1.480 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 250 reflections
θ = 2–22°
μ = 0.112 mm^{-1}
T = 293 (2) K
Prismatic
0.3 × 0.1 × 0.06 mm
Colourless

Data collection

Enraf–Nonius FAST diffractometer
ω scans in 0.2° steps
Absorption correction: none
5215 measured reflections
1875 independent reflections
1541 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0354
θ_{max} = 24.89°
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 11$
$l = -10 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0493
$wR(F^2)$ = 0.1124
S = 0.969
1875 reflections
240 parameters
H atoms riding, U_{iso} refined
$w = 1/[\sigma^2(F_o^2) + (0.1291P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	U_{eq}
N1	−0.0878 (2)	0.8283 (3)	−0.0201 (2)	0.0177 (6)
C2	−0.0158 (3)	0.8987 (3)	0.0608 (2)	0.0183 (8)
O2	0.0318 (2)	0.8405 (2)	0.1410 (2)	0.0232 (5)
N3	−0.0031 (3)	1.0298 (3)	0.0495 (2)	0.0179 (6)
C4	−0.0611 (3)	1.0916 (3)	−0.0364 (3)	0.0171 (7)
N4	−0.0627 (3)	1.2209 (3)	−0.0380 (2)	0.0273 (7)
C5	−0.1159 (3)	1.0206 (3)	−0.1265 (2)	0.0172 (7)
C6	−0.1295 (3)	0.8901 (3)	−0.1147 (2)	0.0163 (7)
C7	−0.1862 (3)	0.8253 (3)	−0.2145 (3)	0.0209 (8)
C8	−0.2018 (4)	0.9385 (3)	−0.2969 (3)	0.0291 (9)
C9	−0.1633 (3)	1.0651 (3)	−0.2384 (3)	0.0230 (8)
C1′	−0.1263 (4)	0.6926 (3)	−0.0010 (3)	0.0212 (8)
C2′	−0.0065 (4)	0.5982 (3)	0.0265 (3)	0.0218 (8)
C3′	−0.0480 (3)	0.5404 (3)	0.1370 (3)	0.0199 (7)
O3′	−0.0104 (2)	0.4071 (2)	0.1433 (2)	0.0277 (6)
O4′	−0.2240 (2)	0.6866 (2)	0.0869 (2)	0.0221 (6)
C4′	−0.2062 (3)	0.5622 (3)	0.1375 (3)	0.0204 (7)
C5′	−0.2788 (3)	0.5585 (3)	0.2481 (3)	0.0235 (8)
O5′	−0.2226 (2)	0.6426 (2)	0.3296 (2)	0.0268 (6)

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

C2—N1—C1′—O4′	64.4 (3)	C1′—O4′—C4′—C3′	39.6 (3)
O4′—C1′—C2′—C3′	0.1 (3)	C2′—C3′—C4′—O4′	−37.8 (3)
C1′—C2′—C3′—C4′	22.4 (3)	O4′—C4′—C5′—O5′	−65.5 (3)
C2′—C1′—O4′—C4′	−24.6 (3)	C3′—C4′—C5′—O5′	53.6 (4)

The assignment of absolute configuration was made on chemical grounds, with the base having a β-configuration with respect to the deoxyribose sugar.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1990); further details from Darr, Drake, Hursthouse & Malik (1993). Cell refinement: *MADNES*. Data reduction: *MADNES*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEX* (McArdle, 1993). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1048). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(*E*)-2,2,5,5-Tetramethyl-3,4-bis[4-(tribromomethyl)phenyl]hex-3-ene

JAMES E. GANO,* KRISTIN KIRSCHBAUM AND PADMANABHAN SEKHER

Department of Chemistry, University of Toledo, Toledo, OH 43606, USA. E-mail: jgano@uoft02.utoledo.edu

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Abstract

Steric repulsion of the *tert*-butyl groups of the title compound, $C_{24}H_{26}Br_6$, causes the phenyl rings to rotate out of the plane of the central double bond eliminating the conjugation between the three π systems, yet the central double bond is normal, 1.33 (1) Å. The molecules pack together to maximize Br···Br and *tert*-butyl···*tert*-butyl interactions forming 'planes' of Br atoms and *tert*-butyl groups. The results are supplemented by MOPAC calculations.

Comment

Stilbenes bearing *tert*-butyl groups on the central C atoms have received significant attention because of their unusual geometry (Gano, Park, Pinkerton & Lenoir, 1990, 1991; Gano, Park, Subramaniam, Lenoir & Gleiter, 1991; Laali, Gano, Lenoir & Gundlach, 1994; Lenoir, Gano & McTague, 1986). Although the crystal structure of a *Z* isomer appeared some time ago (Gano, Park, Pinkerton & Lenoir, 1991), crystallographic information on the *E* isomers has proven to be elusive (Ermer, 1977). Herein is provided the first report of a crystallographic investigation of an (*E*)-di-*tert*-butylstilbene, (*E*)-2,2,5,5-tetramethyl-3,4-bis[4-(tribromomethyl)phenyl]hex-3-ene, (1*a*). Stilbene (1*a*) was prepared by bromination of stilbene (1*b*), whose preparation followed the procedure for preparation of the parent stilbene (1*c*) (Lenoir *et al.*, 1986).

Recrystallization of (1*a*) from chloroform produced crystals suitable for X-ray diffraction measurements. Although the results immediately suggested that additional rotational isomers were needed to accommo-