C3′	0.3459 (11)	0.2374 (4)	0.3239 (8)	0.084 (3)
C3	0.7526 (9)	−0.0830 (3)	0.2699 (7)	0.065 (2)
C4′	0.2078 (11)	0.2280 (4)	0.2495 (8)	0.076 (2)
C4	0.6209 (8)	−0.0979 (3)	0.3351 (6)	0.054 (2)
C5′	0.1640 (7)	0.1669 (3)	0.2047 (5)	0.045 (2)
C5	0.4607 (6)	−0.0685 (2)	0.3150 (5)	0.039 (1)
C6′	0.2708 (6)	0.1152 (2)	0.2402 (5)	0.041 (1)
C6	0.4404 (6)	−0.0231 (3)	0.2272 (5)	0.044 (1)
C7′	0.0123 (8)	0.1593 (2)	0.1224 (6)	0.044 (2)
C7	0.3197 (7)	−0.0882 (2)	0.3885 (5)	0.041 (1)
C8′	−0.1531 (10)	0.1624 (3)	0.1569 (7)	0.064 (2)
C8	0.2566 (8)	−0.1505 (3)	0.3854 (5)	0.046 (2)
C9′	−0.2904 (11)	0.1586 (4)	0.0799 (9)	0.070 (2)
C9	0.1301 (9)	−0.1695 (4)	0.4542 (6)	0.059 (2)
C10′	−0.2728 (11)	0.1505 (3)	−0.0328 (8)	0.065 (2)
C10	0.0653 (9)	−0.1264 (4)	0.5289 (6)	0.062 (2)
C11′	−0.1116 (11)	0.1471 (4)	−0.0689 (8)	0.073 (2)
C11	0.1288 (10)	−0.0653 (4)	0.5341 (6)	0.066 (2)
C12′	0.0294 (9)	0.1513 (3)	0.0084 (6)	0.060 (2)
C12	0.2545 (8)	−0.0451 (3)	0.4660 (5)	0.050 (2)

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

Te—C6	2.105 (5)	C5—C6	1.390 (7)
Te—C6′	2.125 (5)	C5—C7	1.497 (7)
C1′—C2′	1.359 (9)	C7′—C12′	1.360 (8)
C1′—C6′	1.377 (8)	C7′—C8′	1.377 (9)
C1—C2	1.352 (9)	C7—C8	1.374 (7)
C1—C6	1.383 (8)	C7—C12	1.391 (7)
C2′—C3′	1.358 (10)	C8′—C9′	1.352 (11)
C2—C3	1.350 (10)	C8—C9	1.370 (9)
C3′—C4′	1.351 (11)	C9′—C10′	1.347 (11)
C3—C4	1.355 (9)	C9—C10	1.367 (10)
C4′—C5′	1.397 (9)	C10′—C11′	1.353 (11)
C4—C5	1.392 (8)	C10—C11	1.352 (10)
C5′—C6′	1.397 (7)	C11′—C12′	1.376 (10)
C5′—C7′	1.480 (8)	C11—C12	1.368 (9)
C6—Te—C6′	96.2 (2)	C1—C6—Te	117.0 (5)
C2′—C1′—C6′	121.7 (6)	C5—C6—Te	123.7 (4)
C2—C1—C6	121.2 (7)	C12′—C7′—C8′	116.7 (6)
C3′—C2′—C1′	119.4 (7)	C12′—C7′—C5′	121.6 (5)
C3—C2—C1	119.9 (7)	C8′—C7′—C5′	121.6 (6)
C4′—C3′—C2′	120.3 (7)	C8—C7—C12	118.0 (5)
C2—C3—C4	121.0 (7)	C8—C7—C5	120.9 (5)
C3′—C4′—C5′	122.3 (7)	C12—C7—C5	121.0 (5)
C3—C4—C5	120.6 (6)	C9′—C8′—C7′	120.9 (7)
C4′—C5′—C6′	116.8 (6)	C9—C8—C7	121.3 (6)
C4′—C5′—C7′	120.2 (5)	C10′—C9′—C8′	122.1 (9)
C6′—C5′—C7′	123.0 (5)	C10—C9—C8	120.2 (7)
C6—C5—C4	118.3 (5)	C9′—C10′—C11′	118.1 (8)
C6—C5—C7	123.8 (4)	C11—C10—C9	119.0 (6)
C4—C5—C7	117.9 (5)	C10′—C11′—C12′	120.4 (8)
C1′—C6′—C5′	119.5 (5)	C10—C11—C12	122.1 (6)
C1′—C6′—Te	122.9 (4)	C7′—C12′—C11′	121.7 (7)
C5′—C6′—Te	117.6 (4)	C11—C12—C7	119.5 (6)
C1—C6—C5	119.0 (5)		

The structure was determined by direct methods and refined by least squares with anisotropic displacement parameters for the non-H atoms. All H atoms were located from difference Fourier syntheses and were refined isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Program(s) used to solve structure: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1026). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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7-(2′-Deoxy-α-D-ribofuranosyl)hypoxanthine

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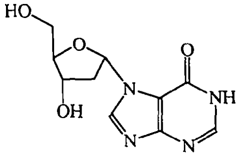
Abstract

The α-configured N7 analogue of 2′-deoxyinosine [7-(2′-deoxy-α-D-ribofuranosyl)hypoxanthine, $C_{10}H_{12}N_4O_4$] shows the following structural characteristics: (i) the furanose part of the molecule adopts the 2′-*endo* conformation [pseudorotation phase angle 166.4 (2)°]; (ii) the torsion angle χ (O4′—C1′—N7—C5) is *syn* [70.9 (1)°] with the base substituent pointing away from the sugar unit; (iii) the nucleobases are not hydrogen bonded to each other; only sugar-base hydrogen bonds between adjacent molecules were detected.

Comment

During studies directed towards the design of oligonucleotide analogues that can form stable triplex structures with native DNA duplexes (for a review see Thuong & Hélène, 1993), we became interested in oligonucleotides built from the title compound, (1). A detailed knowledge of the conformation of the monomeric nucleoside (1) is compulsory to control and refine the initial parameters used in the design of the anticipated triplex structure. Since only three structures of α-ribofuranosides have been reported so far {α-5-acetyl-2′-deoxyuridine (Hamor, O'Leary & Walker, 1977), 5-[1-(2′-deoxy-α-D-ribofuranosyl)uracilyl]disulfide (Shefter, Kotick & Bardos, 1967) and (*S*)-2-amino-9-(2-deoxy-β-D-ribofuransyl)-4-methyl-1,2,4-triazolin-5-one hydrate (Revankar *et al.*, 1990)}, this contribution also helps in determining general structural aspects of this class of nucleosides.



(I)

The sugar fragment of (1) essentially shows the 2′-*endo* envelope conformation with a puckering amplitude of 0.300 (1) Å and a pseudorotation phase angle of 166.4 (2)°. This can easily be seen from the torsion angle ν_4 (C3′—C4′—O4′—C1′) of −2.8 (1)°, implying an almost planar arrangement of these four atoms, and from the positive value of the torsion angle ν_1 (O4′—C1′—C2′—C3′) of 28.9 (1)°. O5′ lies above the centre of the furanoside ring (positive synclinal torsion angle γ) with H51′ and H52′ pointing away from the sugar ring. According to the rules defining conformations in β-nucleosides (Saenger, 1984), the torsion angle χ (O4′—C1′—N7—C5) of 70.9 (1)°, which measures the conformation around the nucleosidic bond, indicates the *syn* arrangement. However, one should note that, as in β-nucleosides with *anti* orientation, the purine base in (1) points away from the sugar. A hydrogen contact between O3′ and H3 of length 2.21 (2) Å could help stabilize this conformation. The base deviates slightly from planarity in a bow fashion. N1, C2, C8 and N7 lie 0.02–0.03 Å below the plane, while all the other atoms lie above the plane, with C4 and N9 having the greatest positive deviation [0.029 (1) and 0.016 (1) Å, respectively]. A search in the Cambridge Structural Database (Allen *et al.*, 1979) for crystal structures containing hypoxanthine yielded two entries for hypoxanthinium nitrate monohydrate (Rosenstein *et al.*, 1982; Schmalle, Hanggi & Dubler, 1990) and hypoxanthine-8-(2′-deoxyriboside) (Ducruix & Pascard-Billy, 1975). Compared with the protonated hypoxanthine (Schmalle *et al.*, 1990), the bond lengths of (1) tend to be slightly longer; the greatest difference is found for the C8—N7 bond (0.03 Å).

In the crystal structure of the title compound the base units are stacked along the crystallographic *a* axis. The two base stacks are related by the crystallographic screw rotation. The distance between the planes of the stacked base units is 3.348 Å. However, the overlap of the bases is only marginal; N7 of one molecule is positioned over N3 of the neighbouring molecule (3.40 Å). Hydrogen bonds between molecules in different stacks (Fig. 2) provide additional crystal stabilization. Three hydrogen bonds are found, O5′—H5′···N3, N1—H1···O5′ and O3′—H3O′···N9 [1.94 (3), 1.99 (2) and 2.02 (3) Å, respectively]. It should be noted that O5′ is doubly hydrogen bonded, once as a donor and once as an acceptor, whereas the carbonyl O atom of the base is not involved in any hydrogen bond at all.

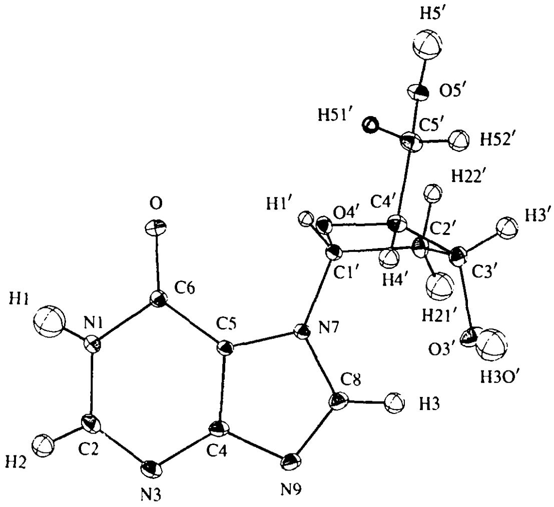


Fig. 1. Molecular structure of (1) showing atomic numbering and 50% probability displacement ellipsoids.

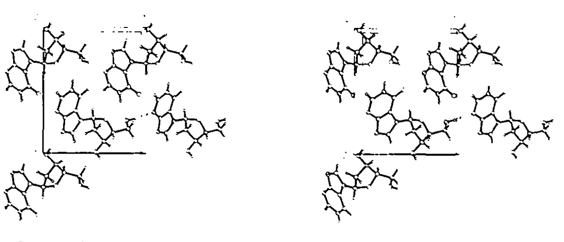


Fig. 2. Packing diagram of (1). Hydrogen bonds are shown as dashed lines.

Experimental

Nucleoside (1) (Marfurt, 1995) was prepared in two steps from methyl-2-deoxy-3,5-diacetyl-D-ribofuranoside and 6-chloropurine in a Lewis acid promoted nucleosidation reaction according to the method of Vorbrüggen & Bennua (1981), followed by hydrolysis of the ester groups and substitution of the 6-chloro substituent by an O atom with 2*M* NaOH. After purification by flash chromatography, compound (1) was crystallized from hot water (Marfurt, 1995). The density D_m was measured by flotation.

Crystal data

$C_{10}H_{12}N_4O_4$
$M_r = 252.2$
Monoclinic
$P2_1$
$a = 4.972\,(1)$ Å
$b = 9.379\,(2)$ Å
$c = 11.326\,(2)$ Å
$\beta = 92.18\,(1)°$
$V = 527.8\,(2)$ Å^3
$Z = 2$
$D_x = 1.587$ Mg m^{-3}
$D_m = 1.56$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 14.0–18.3°$
$\mu = 0.13$ mm^{-1}
$T = 100$ K
Prism
0.27 × 0.18 × 0.18 mm
Transparent, colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
2683 measured reflections
2326 independent reflections
2215 observed reflections [$F > 4\sigma(F)$]

$R_{\rm int} = 0.009$
$\theta_{\rm max} = 29.0°$
$h = -7 \rightarrow 7$
$k = -1 \rightarrow 13$
$l = -1 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: 0.2%

Refinement

Refinement on F
$R = 0.0268$
$wR = 0.0357$
$S = 1.2618$
2215 reflections
210 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + 0.00053F^2]$

$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.427$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.232$ 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 (Å^2)*

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

	x	y	z	$U_{\rm eq}$
C1′	0.7848 (2)	0.5044 (2)	0.72070 (9)	0.0088 (2)
C2′	1.0132 (2)	0.5280 (2)	0.81190 (9)	0.0108 (2)
C3′	0.8871 (2)	0.6201 (2)	0.90610 (9)	0.0112 (2)
O3′	0.7772 (2)	0.5282 (1)	0.99150 (7)	0.0157 (2)
C4′	0.6707 (2)	0.7046 (2)	0.83510 (9)	0.0101 (2)
O4′	0.6164 (2)	0.6250	0.72680 (7)	0.0101 (2)
C5′	0.7461 (2)	0.8552 (2)	0.8031 (1)	0.0127 (2)
O5′	0.9893 (2)	0.8517 (1)	0.73900 (8)	0.0133 (2)
O	0.4705 (2)	0.4529 (1)	0.47850 (7)	0.0138 (2)
N1	0.1515 (2)	0.2772 (1)	0.49650 (8)	0.0109 (2)
C2	0.0326 (2)	0.1713 (2)	0.5577 (1)	0.0115 (2)
N3	0.1015 (2)	0.1318 (1)	0.66530 (8)	0.0118 (2)
C4	0.3093 (2)	0.2098 (2)	0.71410 (9)	0.0100 (2)
C5	0.4381 (2)	0.3197 (2)	0.65790 (9)	0.0085 (2)
C6	0.3688 (2)	0.3599 (2)	0.53890 (9)	0.0091 (2)
N7	0.6267 (2)	0.3735 (1)	0.73900 (7)	0.0089 (2)
C8	0.6011 (2)	0.2944 (2)	0.83840 (9)	0.0114 (2)
N9	0.4139 (2)	0.1940 (1)	0.82730 (8)	0.0122 (2)

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

C1′—C2′	1.522 (1)	N1—C2	1.359 (2)
C1′—O4′	1.411 (1)	N1—C6	1.400 (2)
C1′—N7	1.477 (2)	C2—N3	1.307 (1)
C2′—C3′	1.526 (2)	N3—C4	1.366 (2)
C3′—O3′	1.420 (2)	C4—C5	1.382 (2)
C3′—C4′	1.538 (2)	C4—N9	1.373 (1)
C4′—O4′	1.452 (1)	C5—C6	1.429 (1)
C4′—C5′	1.509 (2)	C5—N7	1.383 (1)
C5′—O5′	1.434 (1)	N7—C8	1.358 (2)
O—C6	1.229 (2)	C8—N9	1.327 (2)
C2′—C1′—O4′	106.2 (1)	N3—C4—C5	124.8 (1)
C2′—C1′—N7	114.4 (1)	N3—C4—N9	125.0 (1)
O4′—C1′—N7	109.86 (8)	C5—C4—N9	110.2 (1)
C1′—C2′—C3′	103.95 (9)	C4—C5—C6	122.1 (1)
C2′—C3′—O3′	108.2 (1)	C4—C5—N7	106.30 (9)
C2′—C3′—C4′	102.94 (8)	C6—C5—N7	131.6 (1)
O3′—C3′—C4′	112.90 (9)	O—C6—N1	122.1 (1)
C3′—C4′—O4′	106.3 (1)	O—C6—C5	128.5 (1)
C3′—C4′—C5′	115.63 (9)	N1—C6—C5	109.4 (1)
O4′—C4′—C5′	108.55 (8)	C1′—N7—C5	124.15 (9)
C1′—O4′—C4′	111.22 (8)	C1′—N7—C8	129.61 (9)
C4′—C5′—O5′	108.8 (1)	C5—N7—C8	105.6 (1)
C2—N1—C6	125.09 (9)	N7—C8—N9	113.37 (9)
N1—C2—N3	125.4 (1)	C4—N9—C8	104.6 (1)
C2—N3—C4	113.1 (1)		
O4′—C1′—C2′—C3′	28.9 (1)	C1′—C2′—C3′—C4′	−29.6 (1)
N7—C1′—C2′—C3′	−92.5 (1)	C2′—C3′—C4′—O4′	20.5 (1)
C2′—C1′—O4′—C4′	−16.4 (1)	C2′—C3′—C4′—C5′	−100.0 (1)
N7—C1′—O4′—C4′	107.85 (9)	O3′—C3′—C4′—O4′	−95.8 (1)
C2′—C1′—N7—C5	−169.7 (1)	O3′—C3′—C4′—C5′	143.6 (1)
C2′—C1′—N7—C8	20.9 (2)	C3′—C4′—O4′—C1′	−2.8 (1)
O4′—C1′—N7—C5	70.9 (1)	C5′—C4′—O4′—C1′	122.15 (9)
O4′—C1′—N7—C8	−98.4 (1)	C3′—C4′—C5′—O5′	56.4 (1)
C1′—C2′—C3′—O3′	90.1 (1)	O4′—C4′—C5′—O5′	−62.9 (1)

The absolute configuration was predetermined from the reactants and could not be determined in the structure solution.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *PEANUT* (Hummel, Hauser & Bürgi, 1990), *SHELXTL/PC*. Software used to prepare material for publication: *PARST* (Nardelli, 1983), *BONDLA* (Dreissig, Doherty, Stewart & Hall, 1992).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1142). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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ap-8-Chloro-1,4-dimethyl-9-(2-methylbenzyl)triptycene and *sc**(9*S**)-8-Chloro-1,4-dimethyl-9-(2-methylbenzyl)triptycene

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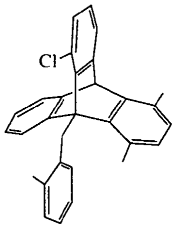
Abstract

Two atropisomers, *ap* and *sc**(9*S**), of the title compound [8-chloro-1,4-dimethyl-9-(2-methylbenzyl)-9,10-dihydro-9,10-*o*-benzenoanthracene, $C_{30}H_{25}Cl$] have been isolated and their structures determined by X-ray diffraction. The structures of the two isomers are essentially the same as those of the analogous bromo derivatives. The crystal of the *sc**(9*S**) isomer decomposed when it was heated to 493 K, owing to the *sc*–*ap* transition.

Comment

Atropisomerism is defined as stereoisomerism due to restricted rotation about a single bond where the isomers can actually be isolated (Eliel, 1962). Kinetic studies of the isomerization of 9-(2-methylbenzyl)triptycene have been reported (Yamamoto, Nemoto & Ohashi, 1992). The dynamic ^{13}C NMR study suggested that the molecule has an energy barrier of 49.6 kJ mol^{-1} for gear rotation of the 2-methylbenzyl group. The introduction of a substituent at the *peri* position was expected to raise the energy barrier enough for atropisomerism to occur. When Cl and Br atoms were introduced at the *peri* position, two stable *ap* and *sc**(9*S**) isomers were isolated for both derivatives. Classical kinetic studies in toluene-d_8 solutions revealed that the isomerization barriers at 350 K are 110.5 and 113.8 kJ mol^{-1} for the chloro and bromo derivatives, respectively. In both derivatives, the *sc**(9*S**) isomer was found to be thermally isomerized to the *ap* isomer in the solid state. The structures of the two isomers of the bromo derivative were determined by X-ray diffraction (Nemoto, Ono, Uchida, Ohashi & Yamamoto, 1994) and confirmed those assumed from the NMR study. However, the crystal of the *sc**(9*S**) isomer decomposed during the transition to the *ap* form, contrary to the assumption made from the appearance of the crystal. In order to confirm the above results, the crystal structures of the two isomers of the chloro derivative, (I), have been determined by X-ray analysis.



(I)

The crystal structure of the *ap* isomer (Fig. 1) has two crystallographically independent molecules (*A* and *B*) and is isomorphous with that of the *ap* isomer of the bromo derivative. On the other hand, the crystal of the *sc**(9*S**) isomer (Fig. 2) has a different structure from that of the bromo derivative and also from that of the *ap* isomer (Fig. 1). As observed in the bromo derivative, the crystal of the *sc**(9*S**) isomer decomposed when it was transformed to the *ap* isomer upon heating. This may suggest that the transformation will proceed with retention of the single-crystal form only if the crystals of the *sc**(9*S**) and *ap* isomers have approximately the same structure.

The molecular structures of both the *ap* and *sc**(9*S**) isomers are shown in Fig. 3; only molecule *A* of the *ap* isomer (*ap-A*) is shown, since the two crystallographically independent molecules have approximately the same conformation. The *sc**(9*S**) molecule has a disordered structure. The Cl atom bonded to C13 appeared in the refinement and is denoted as Cl2. This is a mirror image of the original Cl atom, Cl1. The ratio of Cl1 to Cl2 is 74:26. The 2-methylbenzyl group is