

compound] and minor distortions from planarity at C(6) in the hexamethyl compound. Both molecules show considerable angular asymmetry at C(1), thereby alleviating the clash between C(9) and N(2), with a similar distortion at C(10) in the title molecule helping to separate N(3) and F(4) [C(9)···N(2) 2.76 (1), N(3)···F(4) 2.66 (1) Å]. The tetrafluoropyridine dimensions are unremarkable, showing good agreement with those of the corresponding azoxy compound (Banks, Farhat, Fields, Pritchard & Saleh, 1985). Like the azoxy compound there is intermolecular  $\pi$  interaction between alternate trimethylphenyl and tetrafluoropyridyl rings, which, in the azo case, form infinite columns parallel to **b** generated by the screw axis,  $1-x, \frac{1}{2}+y, 1-z$  [C(4)···C(12) 3.40 (1), C(6)···C(10) 3.41 (1) Å].

The author thanks the SERC for financial support (equipment) and Drs R. E. Banks and A. C. Alty for providing the sample.

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*Acta Cryst.* (1987). **C43**, 131–134

## Structures of 2'-Deoxytubercidin\* (I) and 2'-Deoxytubercidin Dihydrate (II)†

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(Received 25 February 1986; accepted 1 August 1986)

**Abstract.** (I):  $C_{11}H_{14}N_4O_3$ ,  $M_r = 250.3$ , orthorhombic,  $P2_12_12_1$ ,  $a = 10.667$  (3),  $b = 14.997$  (4),  $c = 7.158$  (2) Å,  $V = 1145.1$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.452$  Mg m<sup>-3</sup>,  $Cu K\alpha$ ,  $\lambda = 1.5418$  Å,  $\mu = 0.87$  mm<sup>-1</sup>,  $F(000) = 528$ ,  $T = 295$  K,  $R = 2.7\%$  for 1132 observed reflections. (II):  $C_{11}H_{14}N_4O_3 \cdot 2H_2O$ ,  $M_r = 286.3$ , orthorhombic,  $P2_12_12_1$ ,  $a = 9.676$  (2),  $b = 20.221$  (5),  $c = 6.933$  (2) Å,  $V = 1356.5$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.402$  Mg m<sup>-3</sup>,  $Cu K\alpha$ ,  $\lambda = 1.5418$  Å,  $\mu = 0.90$  mm<sup>-1</sup>,  $F(000) = 608$ ,  $T = 295$  K,  $R = 4.7\%$  for 1318 observed reflections. The bond parameters of the two compounds are almost identical. Although the

packing in the crystals of (I) and (II) is different, the conformations of the two molecules are comparable and similar to that observed in crystalline tubercidin [Abola & Sundaralingam (1973). *Acta Cryst.* **B29**, 697–703]. In (I) the sugar and base moieties form layers which are held together by hydrogen bonding, but with no parallel stacking of the bases. Parallel stacking of the bases occurs in (II) with a base–base separation of  $c/2 = 3.46$  Å. The stacks are separated in the **a** direction by the two water molecules and in the [010] direction by sugar residues. Owing to the additional water molecules, the hydrogen-bonding scheme in (II) is more complex than in (I).

\* 7-(2'-Deoxy- $\beta$ -D-erythro-pentofuranosyl)-7H-pyrrolo[2,3-d]-pyrimidin-4-amine.

† Dedicated to Professor Georg Manecke on the occasion of his 70th birthday.

**Introduction.** Compared with double-helical DNA, the alternating polynucleotide copolymer poly-d(AT) exhibits some unusual physical properties (Scheffer,

Elson & Baldwin, 1968; Riggs, Lin & Wells, 1972; Klug, Jack, Viswamitra, Kennard, Shakked & Steitz, 1979; Viswamitra *et al.*, 1978, 1982; Saenger, 1983). In order to investigate the nature and origin of these peculiarities, the 2'-deoxyadenosine analogue 2'-deoxytubercidin (Fig. 1) was synthesized (Seela & Kehne, 1983), in which N(7) of the base is replaced by a C—H group. In subsequent studies on oligo-d(AT) analogues, 2'-deoxyadenosine was replaced by this compound, and physicochemical and biochemical properties of those oligomers were investigated (Seela & Kehne, 1985). As a first step towards understanding the structural and conformational features of 2'-deoxytubercidin, the crystal structures of its anhydrous and dihydrate modifications were determined and are compared in the present work with the ribo-analogue tubercidin (Stroud, 1973; Abola & Sundaralingham, 1973).

**Experimental.** The nucleoside 2'-deoxytubercidin crystallizes in two modifications. Colorless crystals of the anhydrous form were grown from water, while the dihydrate was obtained from a water-methanol (50/50) solution. Crystal dimensions: 0.15 × 0.3 × 0.5 mm (I) and 0.2 × 0.17 × 0.65 mm (II). The lattice parameters for both compounds were determined from 20 axial reflections of intermediate  $\sin\theta$  range. 1138 and 1333 unique reflections for compounds (I) and (II) measured on a Stoe four-circle diffractometer,  $\omega$ -2 $\theta$  scan mode, stationary background counts on both sides of each scan, Ni-filtered Cu K $\alpha$  radiation,  $9 < 2\theta < 130^\circ$ ; 6 reflections in (I) and 15 in (II) with  $I < 2\sigma(I)$  considered unobserved; data treated for Lorentz and polarization factors but not for absorption; index ranges:  $h$  0–12,  $k$  0–17,  $l$  0–8 in (I),  $h$  0–11,  $k$  0–23,  $l$  0–8 in (II). Structures solved by direct methods (Main *et al.*, 1980), atomic parameters refined by full-matrix least squares isotropically first and then anisotropically. All H atoms located from difference Fourier maps except those of the water molecules in (II) and refined isotropically. Analytical weights used in the final refinement stages as they improved the structures considerably (standard deviations, similarity in equivalent bond parameters *etc.*).

Function minimized  $\sum w|F_o| - |F_c|^2$  with the following weighting scheme:  $w = 0$  if  $|F_c| < 0.66|F_o|$ , else  $w = XY$ , where  $X = 1$  if  $\sin\theta > 0.58$ , else  $w = \sin\theta/0.58$ , and  $Y = 1$  if  $|F_o| < 4.0$ , else  $Y = 4.0/|F_o|$  for compound (I). The same weighting scheme with parameters  $0.5|F_o|$ ,  $\sin\theta = 0.45$  and  $|F_o| = 3.0$  used for compound (II); final  $R$  values are 2.7% ( $wR = 3.5\%$ ) (I) and 4.7% ( $wR = 6.1\%$ ) (II); max.  $\Delta/\sigma$  0.68 and 0.41; max.  $\Delta\rho$  -0.2 to 0.3 and -0.25 to 0.3 e Å<sup>-3</sup> for (I) and (II) respectively; secondary-extinction value  $g = 2.9 \times 10^{-2}$  for (I) and  $1.02 \times 10^{-2}$  for (II). Scattering factors taken from *International Tables for X-ray Crystallography* (1974), corrections for

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å<sup>2</sup> × 10<sup>2</sup>)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
<i>(a) 2'-Deoxytubercidin</i>				
N(1)	0.3705 (2)	0.5020 (1)	0.0461 (3)	4.12 (5)
C(2)	0.4457 (2)	0.4327 (1)	0.0133 (3)	4.09 (6)
N(3)	0.5358 (1)	0.3981 (1)	0.1205 (2)	3.48 (4)
C(4)	0.5470 (2)	0.4417 (1)	0.2842 (2)	2.84 (5)
C(5)	0.4752 (2)	0.5143 (1)	0.3393 (3)	3.11 (5)
C(6)	0.3846 (2)	0.5446 (1)	0.2107 (3)	3.23 (5)
N(6)	0.3130 (2)	0.6162 (1)	0.2431 (3)	4.11 (5)
C(7)	0.5169 (2)	0.5398 (1)	0.5218 (3)	3.97 (6)
C(8)	0.6115 (2)	0.4836 (1)	0.5674 (3)	4.09 (6)
N(9)	0.6323 (1)	0.4237 (1)	0.4226 (2)	3.22 (4)
C(1')	0.7122 (2)	0.3458 (1)	0.4321 (3)	3.04 (5)
C(2')	0.8466 (2)	0.3624 (1)	0.4911 (3)	3.52 (5)
C(3')	0.8822 (2)	0.2723 (1)	0.5735 (3)	3.18 (5)
O(3')	0.9045 (1)	0.2092 (1)	0.4293 (2)	4.22 (5)
C(4')	0.7625 (2)	0.2453 (1)	0.6747 (3)	3.02 (5)
O(4')	0.6623 (1)	0.2865 (1)	0.5704 (2)	3.64 (4)
C(5')	0.7571 (2)	2751 (1)	0.8751 (3)	4.05 (6)
O(5')	0.6428 (2)	0.2479 (1)	0.9580 (2)	4.96 (5)
<i>(b) 2'-Deoxytubercidin dihydrate</i>				
N(1)	0.1599 (3)	0.5792 (1)	0.2381 (5)	3.9 (1)
C(2)	0.0515 (3)	0.5386 (1)	0.2451 (6)	4.5 (1)
N(3)	0.0501 (3)	0.4731 (1)	0.2509 (5)	4.1 (1)
C(4)	0.1780 (3)	0.4476 (1)	0.2475 (5)	3.1 (1)
C(5)	0.3014 (3)	0.4828 (1)	0.2407 (5)	3.3 (1)
C(6)	0.2879 (3)	0.5526 (1)	0.2342 (4)	3.1 (1)
N(6)	0.3957 (3)	0.5936 (1)	0.2249 (5)	4.1 (1)
C(7)	0.4107 (3)	0.4361 (1)	0.2345 (5)	3.8 (1)
C(8)	0.3520 (3)	0.3754 (1)	0.2373 (5)	3.8 (1)
N(9)	0.2098 (3)	0.3811 (1)	0.2465 (4)	3.5 (1)
C(1')	0.1109 (3)	0.3280 (1)	0.2670 (5)	3.7 (1)
C(2')	0.1151 (5)	0.2753 (2)	0.1131 (5)	4.7 (1)
C(3')	0.0594 (3)	0.2143 (1)	0.2144 (5)	3.8 (1)
O(3')	-0.0864 (3)	0.2106 (1)	0.1885 (4)	4.5 (1)
C(4')	0.0974 (3)	0.2265 (1)	0.4270 (5)	3.8 (1)
O(4')	0.1402 (3)	0.2937 (1)	0.4419 (3)	5.4 (1)
C(5')	0.2096 (6)	0.1833 (2)	0.5049 (7)	6.5 (1)
O(5')	0.2289 (4)	0.1925 (1)	0.7091 (5)	6.4 (1)
O(1 $\bar{W}$ )	0.6842 (3)	0.5535 (1)	0.2391 (6)	6.9 (1)
O(2 $\bar{W}$ )	0.7109 (3)	0.5712 (1)	0.6352 (5)	6.3 (1)

anomalous dispersion from Cromer & Liberman (1970). The XRAY76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) was used for all refinement purposes.

**Discussion.** Atomic coordinates of (I) and (II) are given in Table 1.\* Stereoscopic plots of the two molecules with the numbering scheme are shown in Fig. 1. Bond distances and torsion angles of both 2'-deoxytubercidin modifications are compared with data reported for tubercidin (Abola & Sundaralingam, 1973) in Table 2. Bond angles for these three structures have been deposited,\* as have details of the hydrogen-bonding geometries of (I) and (II). Packing arrangements of (I) and (II) are illustrated in Figs. 2 and 3.

In 2'-deoxytubercidin the 2'-hydroxyl group of tubercidin is replaced by an H atom. Therefore bond angles and distances in the base should be affected only

\* Lists of structure factors, anisotropic thermal parameters, H-bond parameters, bond angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43197 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

little. Table 2 shows that even the sugar geometry is virtually unaffected. This is in agreement with a survey (Saenger, 1983) in which ribo- and 2'-deoxyribo-sugar geometries in nucleosides are compared.

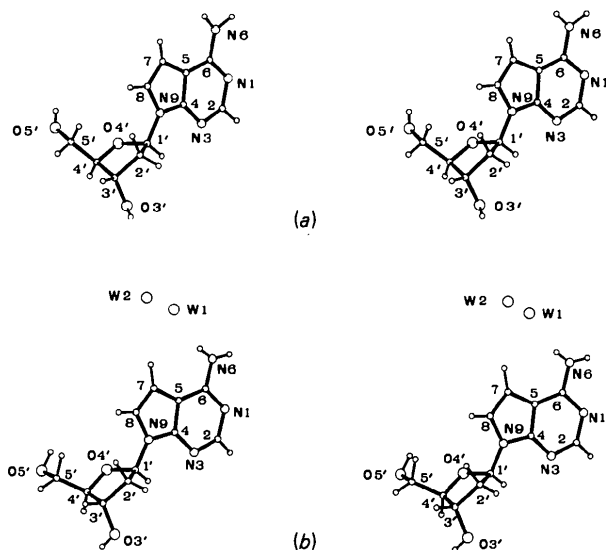


Fig. 1. Stereoscopic ORTEP plots (Johnson, 1965) of (a) compound (I) and (b) compound (II) with numbering scheme.

Table 2. Bond lengths (Å) and torsion angles (°) for 2'-deoxytubercidin compared with data for tubercidin

	2'-Deoxytubercidin		Tubercidin
	anhydrous (I)	dihydrate (II)	(Abola & Sundaralingam, 1973)
N(1)—C(2)	1.333 (3)	1.333 (4)	1.350 (4)
N(1)—C(6)	1.349 (3)	1.351 (4)	1.347 (4)
C(2)—N(3)	1.335 (3)	1.326 (4)	1.329 (4)
N(3)—C(4)	1.348 (2)	1.341 (4)	1.346 (4)
C(4)—C(5)	1.388 (3)	1.391 (4)	1.403 (4)
C(5)—C(6)	1.410 (3)	1.417 (4)	1.406 (4)
C(6)—N(6)	1.338 (3)	1.334 (4)	1.341 (4)
C(5)—C(7)	1.432 (3)	1.419 (4)	1.433 (4)
C(7)—C(8)	1.355 (3)	1.353 (4)	1.359 (4)
C(8)—N(9)	1.389 (3)	1.382 (4)	1.400 (4)
N(9)—C(4)	1.372 (2)	1.379 (4)	1.370 (4)
N(9)—C(1')	1.449 (2)	1.446 (4)	1.438 (4)
C(1')—C(2')	1.515 (3)	1.508 (5)	1.520 (6)
C(2')—C(3')	1.523 (3)	1.518 (5)	1.526 (4)
C(3')—C(4')	1.523 (3)	1.539 (5)	1.527 (5)
C(4')—O(4')	1.442 (2)	1.424 (4)	1.451 (4)
C(1')—O(4')	1.433 (2)	1.426 (4)	1.422 (4)
C(2')—O(2')	—	—	1.401 (4)
C(3')—O(3')	1.420 (3)	1.424 (4)	1.423 (3)
C(4')—C(5')	1.503 (3)	1.495 (6)	1.506 (4)
C(5')—O(5')	1.416 (3)	1.440 (6)	1.421 (5)
C(1')—C(2')—C(3')—C(4')	-38.9 (2)	-27.6 (3)	-36.3 (4)
C(2')—C(3')—C(4')—O(4')	29.7 (2)	11.9 (3)	18.2 (4)
C(3')—C(4')—O(4')—C(1')	-8.2 (2)	9.8 (4)	9.0 (4)
C(4')—O(4')—C(1')—C(2')	-16.9 (2)	-27.7 (4)	-32.9 (4)
O(4')—C(1')—C(2')—C(3')	34.8 (2)	34.1 (4)	43.3 (4)
O(4')—C(4')—C(5')—O(5')	61.9 (2)	66.4 (4)	62.0 (4)
C(3')—C(4')—C(5')—O(5')	179.6 (2)	-173.6 (3)	-178.3 (4)
O(3')—C(3')—C(4')—C(5')	152.7 (2)	133.4 (3)	140.6 (4)
O(4')—C(1')—N(9)—C(8)	62.5 (2)	59.3 (4)	73.0 (4)
O(4')—C(1')—N(9)—C(4)	-104.4 (2)	-115.5 (3)	-112.8 (4)
Pseudorotation parameter P	186.6 (2)	215.1 (3)	149.3

The torsion angles listed in Table 2 show that 2'-deoxytubercidin (I and II) and tubercidin have essentially the same conformation although the crystal packing modes differ widely, as discussed later.

The sugar pucker is C(2')-endo with a minor C(1')-exo component, *i.e.*  ${}^2T_1$ . As illustrated by the torsion angles and pseudorotation parameters given in Table 2, the sugar pucker of tubercidin is more closely related to 2'-deoxytubercidin dihydrate (II) than to the anhydrous form (I). Besides the sugar pucker, the exocyclic torsion angles C(3')—C(4')—C(5')—O(5') and O(4')—C(1')—N(9)—C(4) are nearly the same for all three nucleosides. As the sugar pucker and the two exocyclic torsion angles are sensitive parameters in describing the molecular conformation of nucleosides,

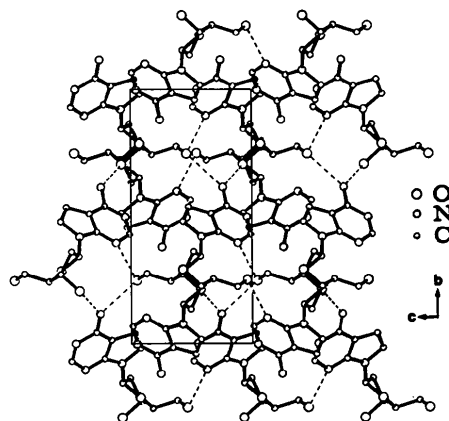


Fig. 2. View of the crystal packing with hydrogen bonding in compound (I), [100] projection.

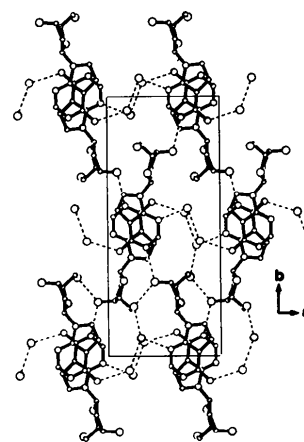


Fig. 3. View of the crystal packing with hydrogen bonding in compound (II), [001] projection.

the preferred occurrence of only one form for two related molecules in three different crystal structures suggests that the conformation of tubercidin or its 2'-deoxy analogue is comparatively 'rigid'.

The crystal structures of tubercidin crystallized from water (Stroud, 1973; Abola & Sundaralingam, 1973) and of anhydrous 2'-deoxytubercidin (I) (Fig. 2) which was also crystallized from water are comparable, whereas the dihydrate (II) differs considerably. As indicated in Fig. 3, the crystal structure of the dihydrate consists of stacked bases along *c*, with a base-base separation of  $c/2 = 3.46 \text{ \AA}$ , a classical value for bases of nucleic acids. The stacks are separated in the *a* direction by two water molecules and in the *b* direction by the sugar moieties. The water molecules, sugar residues and bases are involved in an extended hydrogen-bond network.\* It is unfortunate that the water H atoms could not be located and therefore the hydrogen-bonding scheme is not defined with respect to the water molecules.

In the crystal structures of tubercidin and anhydrous 2'-deoxytubercidin the molecules are arranged such that bases and sugars form layers which are held together by hydrogen bonds. The bases are not stacked parallel to each other as in the dihydrate structure but adjacent bases are tilted in opposite sense about the C(4)–C(5) axis in tubercidin and approximately about the long axis C(8)–C(2) in 2'-deoxytubercidin.

\* See deposition footnote.

*Acta Cryst.* (1987). C43, 134–136

### Structure of 1*H*-Indole-3-ethylensalicylalimine (sal TPA)\*

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(Received 30 April 1986; accepted 24 July 1986)

**Abstract.**  $C_{17}H_{16}N_2O$ ,  $M_r = 264.33$ , orthorhombic,  $Pca2_1$ ,  $a = 15.731(1)$ ,  $b = 6.035(1)$ ,  $c = 14.533(1) \text{ \AA}$ ,  $V = 1379.7(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_m = 1.23$ ,  $D_x = 1.27 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Cu K}\alpha) = 1.5418 \text{ \AA}$ ,  $\mu = 0.599 \text{ mm}^{-1}$ ,  $F(000) = 560$ , room temperature, final

$R = 0.037$  for 691 observed reflections. The present study established the molecular structure of the title compound. Structural features are compared with those of other similar compounds described as radiation protective agents. The C(1)–C(2) bond length of  $1.36(1) \text{ \AA}$  is significantly shorter than a normal aromatic C–C bond. There is an intramolecular hydrogen bond between the phenolic H and the N of the imino group.

\* Systematic name: 2-[2-(1*H*-indol-3-yl)ethyl]iminomethylphenol.

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