However, it opens up by 10° to become greater than the ideal tetrahedral angle in the *cis* S^1—P—S^2—S^3 unit despite the steric requirement of the cyclohexyl groups. This is due to the $S^1 \cdots S^3$ steric interaction becoming important as the molecule approaches an eclipsed configuration. The large valence angle and the low S—P—S—S torsion angle give some measure of the driving force to obtain a completely planar *cis* configuration and hence the strength of the $p\pi$–$d\pi$ interaction.

Under the ideal point symmetry at phosphorus of C_s the filled non-bonding p orbital (or hybrid of π character) on the bridging S atom and the d_{xz} and d_{yz} orbitals on phosphorus transform as A''; thus maximum overlap would take place when the S—P—S—S fragment is planar (torsion angle 0 or 180°). This suggests a mechanism for lowering the *trans* barrier to rotation discussed above. We can think of the barrier as largely due to repulsion of the filled p oribtals on adjacent S atoms (Pauling, 1949). If this electron density is polarized towards phosphorus and away from the S—S bond, the barrier will thus be lowered.

We note that there is nothing unusual about the P—S bond lengths. This suggests that if the π interaction we propose to explain the current structural parameters exists, then it should contribute to all P—S single bonds at tetrahedral phosphorus.

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Structure of 2′-Deoxy-5-azacytidine (Decitabine) Monohydrate

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Abstract. $C_8H_{12}N_4O_4.H_2O$, $M_r = 246{\cdot}2$, monoclinic, $P2_1$, $a = 13{\cdot}487\ (17)$, $b = 7{\cdot}611\ (10)$, $c = 5{\cdot}340\ (1)$ Å, $\beta = 100{\cdot}56\ (1)°$, $V = 538{\cdot}9\ (1{\cdot}4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}52$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}74$ cm^{-1}, $F(000) = 240$, $T = 293$ K, final $R(F) = 0{\cdot}060$, $wR = 0{\cdot}069$ for 578 unique observed $[I > 3\sigma(I)]$ reflections. The structure establishes that decitabine is the β-D-anomer of 2′-deoxy-5-azacytidine, and that the crystals contain a hydrogen-bonded water molecule.

Introduction. Decitabine (1) is believed to be the β-D-anomer of 2′-deoxy-5-azacytidine. It has strong antileukemic properties *in vitro* as well as *in vivo* (Momparler, 1985; Momparler, Rivard & Gyger, 1985). ^{1}H NMR spectroscopy showed only small differences between α- and β-anomers, while various other assignments have also been made (Ben-Hatter & Jiricny, 1986; Piskala & Sorm, 1978; Srivastava, Robbins, Takusagawa & Berman, 1981). It is there-

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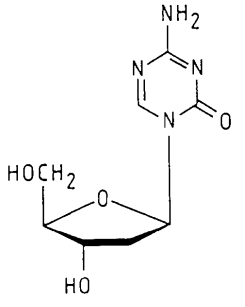
fore necessary to obtain an unequivocal structure of decitabine by diffraction methods.



(1)

Experimental. Decitabine (Pharmachemie BV, batch 14513) was prepared according to a direct glycosylation procedure of silylated 5-azacytosine (Piskala, Synackova, Tomankova, Fiedler & Zizkowsky, 1978). Crystals grown from dimethyl sulfoxide proved to be very hygroscopic, but the aqueous pool left by several such crystals on a glass slide produced good diffraction-quality thin crystalline plates after slow evaporation. A colourless crystal of dimensions 0·1 × 0·43 × 0·008 mm was glued to the end of a glass fibre by epoxy resin. Preliminary X-ray photographs indicated $P2_1$ symmetry; data collection was made on a Stoe Stadi-2 diffractometer. Unit-cell parameters were determined by least-squares refinement of ω-angle measurements of reflections from several layers (Clegg & Sheldrick, 1984). Intensities of 763 reflections in the range $7 \le 2\theta \le 45°$ and h −14→14, k 0→8, l 0→5 measured by a variable ω-scan technique. The data were corrected for Lorentz and polarization effects to give 578 reflections with $I \ge 3\sigma(I)$. No significant decomposition was detected using standard reflections, and no corrections were made for absorption or extinction. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986) and refined by full-matrix least squares (Sheldrick, 1976). H atoms attached to the C atoms were included in calculated positions; one H atom associated with the water O and the two N(4) H atoms were located and refined, but the remaining H atoms could not be found in difference Fourier maps. Final cycles of least-squares refinement of 111 parameters used a weighting scheme $w = 1/[\sigma^2(F) + gF^2]$, $g = 0{\cdot}027$, and gave a final $R = 0{\cdot}060$, $wR = 0{\cdot}069$. In view of the limited data set, only O atoms were given anisotropic thermal parameters. In the last cycle of refinement, $(\Delta/\sigma)_{max}$ was 0·15, and in the final difference Fourier map residual peaks were in the range −0·20 to 0·15 e Å^{-3}. Scattering factors were those included in *SHELX*76.

Table 1. *Fractional atomic coordinates and thermal parameters for non-*H *atoms*

	x	y	z	U_{eq}(Å^2)
O(1)	0·2761 (4)	1·00000	−0·1969 (12)	0·043 (3)*
O(2)	0·2677 (4)	0·5965 (12)	0·2917 (11)	0·036 (3)*
O(3)	0·0465 (5)	0·6891 (12)	0·2834 (14)	0·051 (4)*
O(4)	0·2217 (6)	0·3386 (12)	−0·1058 (13)	0·052 (4)*
O(5)	0·0808 (6)	1·0198 (12)	0·4709 (16)	0·050 (4)*
N(1)	0·3288 (5)	0·7325 (13)	−0·0463 (13)	0·028 (2)
N(2)	0·4056 (4)	0·8772 (13)	−0·3477 (13)	0·029 (2)
N(3)	0·4547 (5)	0·5846 (13)	−0·2062 (13)	0·034 (2)
N(4)	0·5273 (5)	0·7264 (15)	−0·5034 (15)	0·042 (2)
C(1)	0·3362 (6)	0·8768 (14)	−0·2026 (16)	0·029 (2)
C(2)	0·4605 (6)	0·7339 (14)	−0·3516 (15)	0·028 (2)
C(3)	0·3899 (5)	0·5958 (14)	−0·0601 (16)	0·031 (2)
C(4)	0·2499 (5)	0·7340 (15)	0·1197 (15)	0·032 (2)
C(5)	0·1449 (6)	0·7060 (16)	−0·0426 (16)	0·034 (2)
C(6)	0·0946 (6)	0·5862 (16)	0·1194 (17)	0·040 (2)
C(7)	0·1809 (5)	0·4778 (13)	0·2675 (17)	0·031 (2)
C(8)	0·2020 (7)	0·3077 (15)	0·1454 (18)	0·042 (2)

* $U_{eq} = \frac{1}{3}$ trace U.

Table 2. *Bond lengths* (Å) *and angles* (°) *in decitabine*

N(1)—C(1)	1·394 (11)	N(2)—C(1)	1·320 (10)
O(1)—C(1)	1·243 (10)	N(2)—C(2)	1·320 (12)
N(3)—C(2)	1·387 (12)	N(4)—C(2)	1·318 (12)
N(1)—C(3)	1·337 (11)	N(3)—C(3)	1·277 (10)
C(5)—C(4)	1·533 (11)	N(1)—C(4)	1·505 (10)
O(2)—C(4)	1·383 (11)	C(6)—C(5)	1·502 (14)
C(7)—C(6)	1·524 (12)	O(3)—C(6)	1·418 (11)
C(8)—C(7)	1·500 (14)	O(2)—C(7)	1·466 (9)
O(4)—C(8)	1·434 (12)		
N(2)—C(1)—N(1)	119·3 (7)	O(1)—C(1)—N(1)	117·5 (7)
O(1)—C(1)—N(2)	123·3 (8)	N(3)—C(2)—N(2)	125·3 (7)
N(4)—C(2)—N(2)	119·6 (8)	N(4)—C(2)—N(3)	115·1 (8)
N(3)—C(3)—N(1)	125·7 (8)	N(1)—C(4)—C(5)	110·2 (6)
O(2)—C(4)—C(5)	107·5 (7)	O(2)—C(4)—N(1)	109·3 (6)
C(6)—C(5)—C(4)	103·1 (7)	C(7)—C(6)—C(5)	104·2 (7)
O(3)—C(6)—C(5)	109·1 (8)	O(3)—C(6)—C(7)	111·8 (8)
C(8)—C(7)—C(6)	115·4 (8)	O(2)—C(7)—C(6)	103·5 (7)
O(2)—C(7)—C(8)	111·0 (6)	O(4)—C(8)—C(7)	110·4 (8)
C(3)—N(1)—C(1)	117·9 (6)	C(4)—N(1)—C(1)	118·9 (6)
C(4)—N(1)—C(3)	123·2 (7)	C(2)—N(2)—C(1)	117·9 (8)
C(3)—N(3)—C(2)	113·8 (8)	C(7)—O(2)—C(4)	111·7 (5)

Discussion. The atomic coordinates and U_{eq} values for non-H atoms are listed in Table 1.* Bond lengths and angles are given in Table 2. The molecular structure is shown in Fig. 1.

The configuration at the C(6) and C(7) atoms of the deoxyribose ring is known from the 5-azacytosine used in the preparation. Consequently, the X-ray structure establishes the R configuration for C(4), and hence that decitabine is the β-D-anomer of 2′-deoxy-5-azacytidine.

Bond lengths within the azacytosine ring suggest considerable delocalization, in particular the bond length C(1)—N(2) which is formally single, is similar to the formal double-bond distance C(2)—N(2). However, the limited accuracy of individual bond

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53634 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

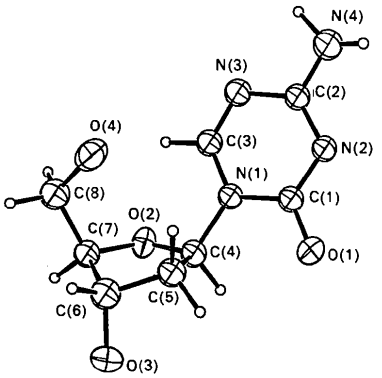


Fig. 1. Molecular structure for decitabine showing 50% probability thermal ellipsoids for the non-H atoms, and the atom-numbering scheme. H atoms on O(3) and O(4) were not located.

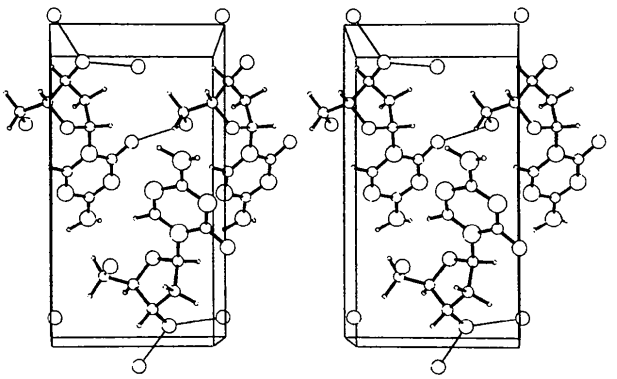


Fig. 2. Stereoscopic view of the unit-cell contents of decitabine monohydrate. Short O···O contacts involved in H bonding are shown by thin connecting lines.

lengths, arising from the small size of the data set, precludes detailed comparison with related systems.

The packing of the molecules is shown in Fig. 2. There appears to be an intermolecular H bond between O(4) and O(1) at $(x, y-1, z)$; the O···O distance is 2·747 (12) Å. The single water molecule, which appears to be crucial for non-hygroscopic crystal formation, is involved in H bonding to two O(3) atoms from different molecules; O(5)···O(3) is 2·717 (11) Å and O(5)···O(3) at $(-x, \frac{1}{2}+y, 1-z)$ is 2·676 (11) Å. The single H atom attached to the water O atom, which was located in a difference Fourier map, refined satisfactorily giving a O(5)—H(5) distance of 0·79 (8) Å. It does not lie along the short O(5)···O(3) vectors listed above, but lies along the vector to O(1) at $(x, y, 1+z)$; this O···O vector is 2·897 (9) Å in length. It is curious that no H atoms corresponding to the second water H, or attached to O(3) and O(4), could be located even though all other H atoms gave significant peaks in difference Fourier maps.

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Structure of Diprotonated DL-Histidinium Dinitrate

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Abstract. $C_6H_{11}N_3O_2^{2+}.2NO_3^-$, $M_r = 281{\cdot}18$, monoclinic, $P2_1/a$, $a = 8{\cdot}370\ (2)$, $b = 14{\cdot}973\ (3)$, $c = 9{\cdot}342\ (2)$ Å, $\beta = 100{\cdot}69\ (2)°$, $V = 1150\ (1)$ Å^3, $Z = 4$, $D_m = 1{\cdot}622$ (flotation), $D_x = 1{\cdot}623$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1{\cdot}62$ cm^{-1}, $F(000) = 584$, $T = 293$ K, $R = 0{\cdot}035$, $wR = 0{\cdot}037$ for 1104

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