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The Crystal Structure of 2,2′-Anhydro-2-hydroxy-1-(β-D-*arabino*-pentofuranosyl)-4-pyridone

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$C_{10}H_{11}NO_5$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}255\,(3)$, $b = 16{\cdot}783\,(5)$, $c = 12{\cdot}858\,(4)$ Å, $Z = 8$, $D_c = 1{\cdot}485$ g cm^{-3}, $\bar{\mu}$(Mo $K\alpha$) = 1·59 cm^{-1}. The structure was determined by direct methods and refined by full-matrix least squares to $R = 0{\cdot}05$ [1476 reflexions with $I \geq 3\sigma(I)$; 73% of total in the sphere $3° \geq 2\theta \geq 50°$]. There are two molecules in the asymmetric unit; one has the E_4 [C(4′)-*exo*] conformation, the other the ^4E [C(4′)-*endo*]. Ring fusion has fixed the glycosidic torsion angle (average $\chi_{CN} = 292{\cdot}0°$) but the torsion angles about C(4′)—C(5′) are different (molecule *A*: $\varphi_{OO} = 69{\cdot}5°$, $\varphi_{OC} = 174{\cdot}2°$; molecule *B*: $\varphi_{OO} = 169{\cdot}9°$, $\varphi_{OC} = 71{\cdot}8°$).

Introduction

Several 3-deazapyrimidines possess significant antitumour activities, although their mechanism of action is not fully elucidated. Implicit in their activity is the lack of an N atom in the 3 position of the pyrimidine ring, thus precluding Watson–Crick base pairing. A comparison of the molecular geometry of the present compound with that of the related 2,2′-anhydro-1-(β-D-*arabino*-furanosyl)uracil (Delbaere & James, 1973) is made in this paper.

Suitable single crystals of the title compound were obtained from Dr M. J. Robins, Chemistry Department, University of Alberta. The compound had been synthesized according to Robins & Currie (1968). The space group was determined from the systematic absences observed on photographs ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$) and the final cell dimensions and intensities were measured from a crystal (0·40 × 0·25 × 0·10 mm) with a FACS-1 diffractometer. Details of the data collection are those described in Hutcheon & James (1974). Those reflexions with $\sigma(I)/I > 0{\cdot}30$ were excluded from the solution and refinement. The standard deviation in intensity was computed from $\sigma(I) = [P + t^2B + (0{\cdot}01I)^2]^{1/2}$, where P is the total peak count, B the total background count, I the net intensity of the peak and t the ratio of the total peak-scan time to the total background-counting time. No corrections for absorption were applied.

The structure was solved by symbolic addition (Karle & Karle, 1966) and tangent refinement (Karle & Hauptman, 1956). Those Σ_2 relations which resulted from three reflexions on the same axial zone were removed (Karle, 1969). Completion of the initial model was achieved by a series of F_o maps based on partial structural information from the starting E map. Full-matrix least-squares refinement of all the atomic

Table 1. *Final atomic parameters* ($\times 10^4$, *for* H $\times 10^3$) *with standard deviations in parentheses*

	x	y	z		x	y	z
N(1)*A*	27 (7)	3399 (3)	3566 (4)	N(1)*B*	5511 (9)	3253 (3)	1649 (4)
C(2)*A*	546 (9)	3214 (4)	2605 (5)	C(2)*B*	5823 (8)	3145 (4)	633 (5)
C(3)*A*	89 (9)	3582 (4)	1728 (5)	C(3)*B*	5305 (9)	3617 (4)	−127 (5)
C(4)*A*	−1030 (9)	4174 (4)	1802 (5)	C(4)*B*	4374 (9)	4268 (4)	149 (6)
O(4)*A*	−1569 (8)	4501 (3)	1018 (4)	O(4)*B*	3856 (7)	4734 (3)	−534 (4)
C(5)*A*	−1511 (10)	4369 (4)	2843 (5)	C(5)*B*	4062 (11)	4364 (5)	1235 (7)
C(6)*A*	−997 (10)	3980 (3)	3676 (5)	C(6)*B*	4630 (11)	3871 (5)	1947 (6)
C(1′)*A*	566 (9)	2843 (4)	4338 (5)	C(1′)*B*	6225 (9)	2656 (4)	2310 (5)
C(2′)*A*	1704 (10)	2363 (4)	3722 (5)	C(2′)*B*	7146 (9)	2191 (4)	1510 (5)
O(2′)*A*	1556 (7)	2637 (3)	2651 (4)	O(2′)*B*	6712 (7)	2518 (2)	490 (3)
C(3′)*A*	1228 (9)	1496 (3)	3857 (4)	C(3′)*B*	6633 (8)	1331 (4)	1628 (5)
O(3′)*A*	2454 (7)	1018 (3)	4053 (4)	O(3′)*B*	7645 (7)	914 (4)	2253 (4)
C(4′)*A*	145 (9)	1547 (4)	4752 (5)	C(4′)*B*	5164 (9)	1395 (4)	2202 (5)
O(1′)*A*	−534 (6)	2301 (2)	4620 (4)	O(1′)*B*	5245 (8)	2128 (3)	2786 (4)
C(5′)*A*	−1005 (8)	895 (4)	4734 (5)	C(5′)*B*	3911 (10)	1385 (5)	1459 (6)
O(5′)*A*	−1851 (6)	956 (3)	5652 (4)	O(5′)*B*	3763 (9)	611 (3)	1065 (5)
H(3)*A*	40 (9)	343 (4)	109 (6)	H(3)*B*	557 (13)	352 (6)	−83 (8)
H(5)*A*	−204 (15)	481 (6)	296 (9)	H(5)*B*	362 (12)	485 (5)	142 (6)
H(6)*A*	−128 (19)	412 (8)	432 (11)	H(6)*B*	446 (13)	390 (5)	247 (7)
H(1′)*A*	91 (14)	308 (7)	49 (9)	H(1′)*B*	673 (20)	294 (8)	297 (10)
H(2′)*A*	275 (12)	244 (4)	399 (6)	H(2′)*B*	837 (17)	228 (6)	155 (8)
H(3′)*A*	66 (11)	135 (4)	315 (6)	H(3′)*B*	652 (13)	108 (6)	92 (8)
H(3′1)*A*	228 (12)	59 (5)	388 (7)	H(3′1)*B*	804 (12)	62 (5)	189 (7)
H(4′)*A*	67 (12)	155 (5)	545 (7)	H(4′)*B*	505 (16)	86 (6)	284 (9)
H(5′)*A*	−37 (11)	34 (4)	471 (6)	H(5′)*B*	305 (18)	149 (6)	185 (8)
H(5′1)*A*	−156 (15)	88 (6)	403 (8)	H(5′1)*B*	403 (9)	182 (4)	86 (5)
H(5′2)*A*	−252 (14)	55 (6)	564 (8)	H(5′2)*B*	357 (15)	66 (6)	17 (9)

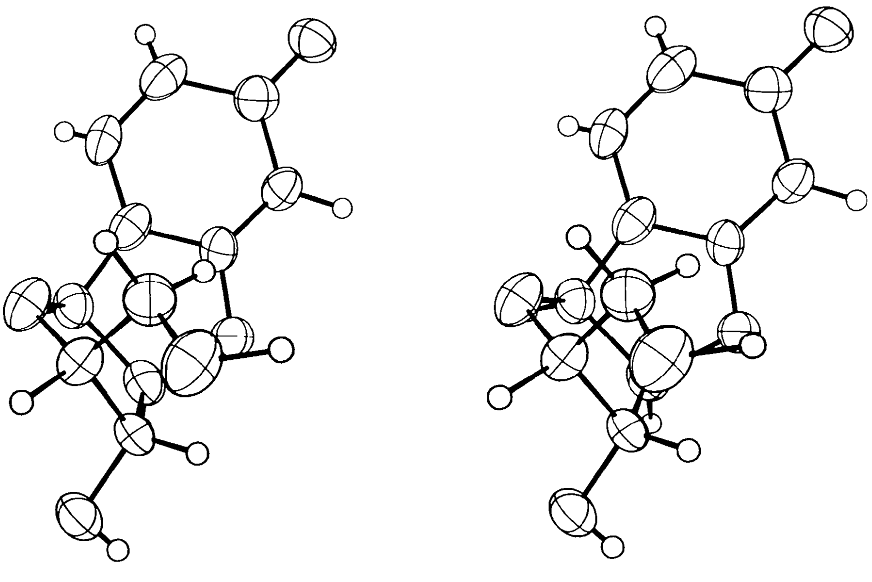


Fig. 1. Stereo-drawing (Johnson, 1965) of molecule *B* in this structure. The sugar pucker is ^4E and the conformation around C(4′)—C(5′) is *trans–gauche*.

parameters converged to a final $R = 0\cdot 05$.* The final cycles minimized $\Sigma\, w(|F_o| - |F_c|)^2$ and the weights were derived from counting statistics, $w^{1/2} = \{2F_o/[P + t^2 B + (0\cdot 01I)^2]\}^{1/2}$. The atomic form factors for C, N and O were those of Cromer & Mann (1968), and for H we used the orbitally contracted model given by Mason & Robertson (1966). The positional parameters are listed in Table 1.

Discussion

The overall conformation of *B* is shown in Fig. 1. A major conformational difference between the two molecules of the asymmetric unit is in the torsion angles about C(4′)–C(5′), which in *A* is *gauche–trans* (φ_{OO} = 69·5°, φ_{OC} = 174·2°) but in *B* is *trans–gauche* (φ_{OO} = 169·9°, φ_{OC} = 71·8°). Coupled with this difference is the difference in sugar pucker; *A* has E_4 [C(4′)-*exo*] whereas *B* has ^4E [C(4′)-*endo*]. (See Table 2 for the details of the out-of-plane displacements of the various atoms.) In 2,2′-anhydro-1-(β-D-*arabino*-furanosyl)-uracil (Delbaere & James, 1973) both molecules in the asymmetric unit had a similar sugar ring pucker C(3′)-*exo*, C(2′)-*exo*, and both had the *gauche–trans* conformation about C(4′)–C(5′). The latter sugar pucker is very similar to the ^4E conformation of *B* in the present structure, which indicates that the conformation of the sugar ring and the C(4′)–C(5′) torsion angle are independent conformational variables. Clearly the major effects on the torsion angles, C(4′)–C(5′), are the hydrogen-bonding characteristics from neighbouring molecules. The cyclic fusion of the base to the sugar ring

Table 2. *Deviations* (Å) *of atoms from the least-squares planes*

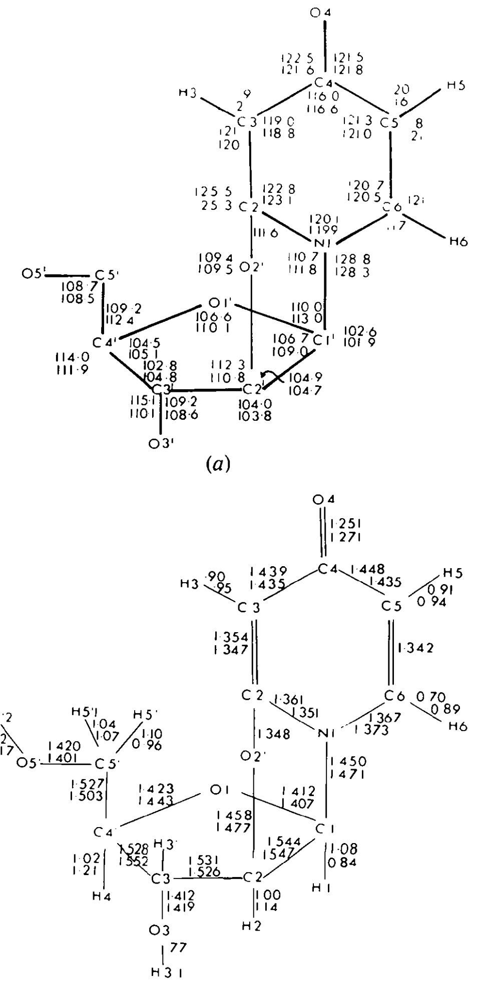
Atoms indicated by an asterisk are those determining the best planes.

	Plane I (Molecule *A*)	Plane II (Molecule *B*)
N(1)*	−0·009	−0·002
C(2)*	−0·001	−0·001
C(3)*	0·018	0·001
C(4)*	−0·024	0·001
C(5)*	0·015	−0·004
C(6)*	0·002	0·005
O(4)	−0·097	0·006
C(1′)	−0·208	0·003
C(2′)	−0·088	0·120
O(2′)	−0·003	0·008
χ^2	11·7	0·45
	Plane III (Molecule *A*)	Plane IV (Molecule *B*)
C(1′)*	0·051	0·018
C(2′)*	−0·048	−0·017
C(3′)*	0·031	0·011
O(1′)*	−0·035	−0·012
C(4′)	0·539	−0·400
C(5′)	0·111	−1·878
O(5′)	0·746	−2·114
N(1)	−1·146	−1·201
O(2′)	−1·355	−1·316
O(3′)	0·880	1·335
χ^2	177·1	21·6

Equations of least-squares planes in direct space

$$Px + Qy + Rz = S$$

Plane	*P*	*Q*	*R*	*S* (Å)
I	6·612	11·634	1·230	4·420
II	7·368	10·035	1·185	7·521
III	4·486	−1·643	11·176	4·576
IV	6·264	−2·746	9·228	5·281



(*a*)

(*b*)

Fig. 2. (*a*) Bond lengths (Å) and (*b*) bond angles (°) and atomic numbering of the title compound. The uppermost number in each pair refers to that dimension of molecule *A*, the lower to *B*. Where there is only one number both dimensions are identical. The e.s.d.'s in bond lengths average 0·009 Å and in bond angles 0·5°.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32436 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

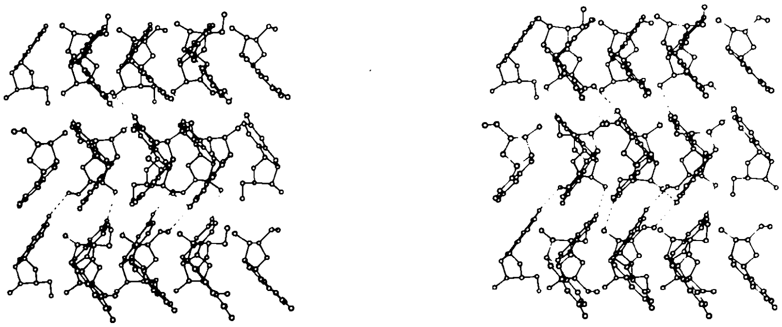

Fig. 3. Stereo-drawing (Johnson, 1965) of the molecular packing of 2,2′-anhydro-2-hydroxy-1-(β-D-*arabino*-pentofuranosyl)-4-pyridone. This view is down [001] with **a** horizontal and **b** vertical. Hydrogen bonds are indicated by dashed lines.

Table 3. *Hydrogen-bond distances and angles*

Bond type A–H···B	Distances (Å) A···B	 A–H	 H···B	Angle (°) A–H···B	Symmetry of acceptor
O(5′)B–H(5′2)···O(4)A	2·701 (7)	1·14 (11)	1·58 (11)	172	$2_1\|\mathbf{a}$
O(3′)B–H(3′1)···O(4)B	2·702 (7)	0·98 (9)	1·92 (13)	151	$2_1\|\mathbf{a}$
O(3′)A–H(3′1)···O(4)A	2·675 (6)	0·77 (9)	1·93 (9)	163	$2_1\|\mathbf{b}$
O(5′)A–H(5′2)···O(4)B	2·763 (7)	0·83 (11)	1·94 (11)	171	$2_1\|\mathbf{b}$

restricts the glycosidic torsion angle χ_{CN} (Sundaralingam, 1969) to 292·0° (average for A and B). This value is similar to the average of 292·2° found in the N(3) analogue of the present structure (Delbaere & James, 1973) and to the value of 299° for 2,2′-anhydro-1-(β-D-*arabino*-furanosyl)cytosine hydrochloride (Brennan & Sundaralingam, 1973).

Table 2 also shows the details of the planarity of the 4-pyridone rings when fused *via* O(2) to C(2′) of the arabinose moiety. The main difference between the two molecules is in the relatively large displacement of C(1′) from the base in A (0·208 Å), whereas the atom furthest from the plane of the base in B is C(2′) (0·120 Å). In 2,2′-anhydro-1-(β-D-*arabino*-furanosyl)uracil the atom furthest from the plane of the base was C(1′) (0·11 Å mean value).

The bond lengths and angles with the atomic numbering are given in Fig. 2. The five-membered ring, C(1′)–N(1)–C(2)–O(2′)–C(2′), has almost the identical geometry as the N(3) analogue (Delbaere & James, 1973). There is considerable double-bond character in C(2)–O(2′), average value 1·348 Å, and this is consistent with the other structures having this 2,2′-anhydro linkage. There are significant differences in the geometry of the base in the bonds involving C(3′), but these differences are consistent with the substitution of N(3) in uracil for the C(3)–H group in the present structure. The bond lengths and angles of the arabinose ring are in agreement with those observed in the other 2,2′-anhydro structures.

The molecular packing is shown in Fig. 3. In 2,2′-anhydro-1-(β-D-*arabino*-furanosyl)uracil (Delbaere & James, 1973) the dominant feature was the dimeric packing of the two independent molecules of the asymmetric unit. In the present crystals, however, the packing is completely different. The two molecules are related by translations of approximately 0·5 in a and 0·17 in c, and are connected by an intricate network of intermolecular hydrogen bonds (Table 3). Hydrogen bonding from O(3′)A to O(4)A and from O(5′)A to O(4)B serves to hold each layer [parallel to (001)] of molecules together, whereas hydrogen bonding from O(3′)B to O(4)B and from O(5′)B to O(4)A holds these molecular layers together. O(4) of each A and B acts as an acceptor of two hydrogen bonds (Table 3). The major conformational differences between A and B are determined by the intermolecular hydrogen bonding [O(5′) of A acts as a donor for an intralayer hydrogen bond, whereas O(5′) of B is a donor for an interlayer hydrogen bond]. Two of the four hydrogen bonds deviate significantly from linearity (∠O–H···O, 151 and 163°) but lie within the allowable range suggested by Donohue (1968).

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Structure Cristalline de l'Iodure de Phénylamino-1 *N*-Pipéridiniométhyl-4 Benzène

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The three-dimensional structure of 1-phenylamino-4-*N*-piperidiniomethylbenzene iodide has been solved by X-ray crystallographic analysis. Crystal data are: space group $P2_1/c$, $Z = 4$, $a = 11{\cdot}41$ (2), $b = 8{\cdot}88$ (7), $c = 18{\cdot}59$ (0) Å, $\beta = 103{\cdot}52°$. The structure was determined by the heavy-atom method. The final R value is 0·061. The iodide anion is responsible for crystalline cohesion.

Introduction

Au cours de travaux concernant l'aminométhylation (Miocque & Vierfond, 1970*a*,*b*), il a été établi par des regroupements chimiques et grâce à l'étude des spectres de ^{1}H RMN que l'aminométhylation des mono- et dialkylanilines porte sur la position *para* du noyau benzénique.

L'extension des recherches à la diphénylamine a montré que la substitution était également possible; elle peut s'effectuer théoriquement soit en *ortho*, soit en *para* de l'azote.

Toutefois, l'abondance des protons aromatiques dans les spectres de ^{1}H RMN des dérivés étudiés, ne permet pas d'établir avec certitude l'emplacement du substituant aminométhyle. Compte tenu de l'intérêt pharmacologique potentiel de ces composés, il a donc semblé utile de déterminer leur structure tridimensionnelle par diffraction des rayons X.

Partie expérimentale

L'iodure de phénylamino-1 *N*-pipéridiniométhyl-4 benzène cristallise dans l'éthanol sous forme de petits prismes monocliniques jaune d'or.

Les valeurs approchées des paramètres cristallins ont été déterminées sur les diagrammes de Bragg et de Weissenberg. Nous les avons précisés lors des mesures au diffractomètre.

Données cristallographiques

Système monoclinique, $a = 11{,}41$ (2), $b = 8{,}88$ (7), $c = 18{,}59$ (0) Å, $\beta = 103{,}52°$, $V = 1833{,}12$ Å^3; $D_c = 1{,}479$, $D_m = 1{,}460$ g cm^{-3}, $Z = 4$. Nombre de réflexions: 2641, dont 2105 observées.

Les intensités diffractées ont été mesurées sur un diffractomètre automatique Siemens équipé d'un compteur à scintillation, en balayage θ–2θ et en utilisant le rayonnement Cu $K\alpha$.