

## Structures of 1-(2,3-Dideoxy-erythro- $\alpha$ -D-hexopyranosyl)thymine and the 1-(2,3-Dideoxy-erythro- $\beta$ -D-hexopyranosyl)thymine.Dioxane Complex\*

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**Abstract.** (I) 1-(2,3-Dideoxy-erythro- $\alpha$ -D-hexopyranosyl)thymine,  $C_{11}H_{16}N_2O_5$ ,  $M_r = 256.26$ , orthorhombic,  $P2_12_12_1$ ,  $a = 4.871$  (2),  $b = 13.182$  (7),  $c = 18.678$  (9) Å,  $V = 1199$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.43$ ,  $D_x = 1.419$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.106$  mm<sup>-1</sup>,  $F(000) = 544$ , room temperature, final  $R = 0.032$  for 1197 unique observed [ $F \geq 4\sigma(F)$ ] reflections. (II) 1-(2,3-Dideoxy-erythro- $\beta$ -D-hexopyranosyl)thymine.dioxane complex,  $C_{11}H_{16}N_2O_5 \cdot C_4H_8O_2$ ,  $M_r = 344.36$ , monoclinic,  $C2$ ,  $a = 17.23$  (1),  $b = 7.651$  (4),  $c = 13.401$  (8) Å,  $\beta = 101.14$  (5)°,  $V = 1734$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.32$ ,  $D_x = 1.320$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.098$  mm<sup>-1</sup>,  $F(000) = 736$ , room temperature, final  $R = 0.048$  for 1704 unique observed [ $F \geq 4\sigma(F)$ ] reflections. In both structures the pyranose ring adopts a chair conformation flattened at the C(4') and C(1') apex for (I) and (II) respectively. For compound (I), with an intramolecular hydrogen bond between O(55')—H(1) and O(2), the H(1)—O(55')—C(55')—C(5') torsion angle is  $-sc$  (synclinal), while in compound (II), where no intramolecular hydrogen bonds are present, this torsion angle is in a  $+sc$  orientation. The  $N$ -glycosidic torsion angle  $\chi$  is  $+sc$  and  $-ac$  (anticlinal) for (I) and (II) respectively. The dioxane molecule in (II) is suspected to be disordered. The packing of both crystals is determined by intermolecular hydrogen bonds. The conformational parameters are in accordance with the IUPAC–IUB Joint Commission on Biochemical Nomenclature [*Pure Appl. Chem.* (1983), **55**, 1273–1280] guidelines.

**Experimental.** Transparent colourless crystals obtained at room temperature, (I) from methanol

and (II) from methanol–dioxane. Density measured by flotation in  $n$ -heptane/ $CCl_4$ . Space groups determined from systematic absences. Data collected on a Stoe STADI-4 four-circle diffractometer, experimental details are set out in Table 1. Standard reflections measured every 2 h, showing for (I) only statistical fluctuations, and for (II) a linear decrease of  $-3.8\%$  for which the intensities have been corrected. Data reduction with a locally modified version of REDU4 (Stoe & Co., 1985), Lorentz and polarization corrections were applied, absorption corrections were unnecessary owing to the small absorption coefficients. Scattering factors were taken from Cromer & Waber (1974) and for H atoms from Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections were included for all non-H atoms (Ibers & Hamilton, 1964). Structure (I) solved with MULTAN82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) which revealed all of the non-H atoms. Refinement on  $F$  by full-matrix least squares, first with isotropic temperature factors and then anisotropically. All H atoms were found in a difference synthesis and included in the refinement with a fixed temperature factor  $B = 4.0$  Å<sup>2</sup>. Since MULTAN82 failed to solve structure (II), the 1-methylthymine skeleton was used as input for the vector-search rotation program ORIENT (Beurskens, Beurskens, Strumpel & Nordman, 1987) and the oriented fragment was subsequently used as input for TRADIR (Doesburg & Beurskens, 1983) to place the fragment in its correct position in the unit cell. The final model was then used as input for DIRDIF (Beurskens, Bosman, Doesburg, van den Hark, Prick, Noordik, Beurskens, Gould & Parthasarathi, 1983) which revealed all of the non-H atoms, including those of the dioxane solvent molecule. Refinement on  $F$  by full-matrix least squares, first with isotropic temperature factors and

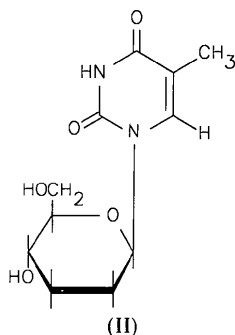
\* Structural Studies of Modified Nucleosides. Part VIII. Part VII: De Winter, Peeters, Blaton, De Ranter, Van Aerschot & Herdewijn (1991).

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Table 1. *Experimental data*

	(I)	(II)
Enantiomer	$\alpha$	$\beta$
Space group	$P2_12_12_1$	$C2$
Crystal dimensions (mm)	$0.2 \times 0.4 \times 0.5$	$0.2 \times 0.5 \times 0.7$
Lattice parameters		
Number of reflections	28	28
$2\theta$ range ( $^\circ$ )	$20 \leq 2\theta \leq 25$	$20 \leq 2\theta \leq 30$
Scan technique	$\omega/2\theta$	$\omega/2\theta$
Maximum $2\theta$ ( $^\circ$ )	55	55
$hkl$ range	$-6 \leq h \leq 0$ $-17 \leq k \leq 0$ $0 \leq l \leq 24$	$-22 \leq h \leq 22$ $0 \leq k \leq 10$ $-17 \leq l \leq 17$
Standard reflections	$0\bar{2}0, 102$	$311, 020$
Number of measured reflections	1657	4416
Number of unique reflections	1633	2138
Number of unique observed reflections [ $F \geq 4\sigma(F)$ ]	1197	1704
$R_{int}$ on $F$ for equivalent observed reflections	—	0.014
$R, wR$	0.032, 0.039	0.048, 0.067
Goodness-of-fit, $S$	1.31	2.06
Weighting scheme	$w = 1/[\sigma(F_o)]^2$	$w = 1/[\sigma(F_o)]^2$
Max. shift/e.s.d.	0.03	0.33
Min. and max. residual electron density ( $e \text{ \AA}^{-3}$ )	$-0.17, +0.14$	$-0.27, +0.37$ (near dioxane)
Number of refined parameters	211	264
Number of reflections per refined parameter	5.7	6.4
Absorption coefficient $\mu$ ( $\text{mm}^{-1}$ )	0.106	0.098

then anisotropically. The nucleoside H atoms were found in a difference synthesis and included in the refinement with fixed temperature factors  $B$  1.3 times the  $B_{eq}$  of the parent atoms, while the dioxane H atoms were placed at their calculated positions with a riding distance of 0.95 Å and with fixed temperature factors  $B$  1.3 times the  $B_{eq}$  of the parent atoms. All calculations were performed on a Digital PDP-11/73 and MicroVAX 2000 microcomputer using *SDP* (Enraf-Nonius, 1985) and *PARST* (Nardelli, 1983).



**Discussion.** The structural formula of the  $\beta$  enantiomer, (II), is shown in the scheme. A *PLUTO* (Motherwell & Clegg, 1978) view of the title compounds with the atomic numbering scheme is shown in Fig. 1. The final atomic coordinates and equivalent isotropic thermal parameters are given in Table

2.\* Bond lengths, bond angles and selected torsion angles are given in Table 3. All bond lengths and bond angles of both nucleosides are within the normal range (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The O(5')—C(1') bond lengths in both molecules are 0.026 (4) (I) and 0.024 (5) Å (II) shorter than the C(5')—O(5') bond lengths. This is in accordance with the corresponding bond lengths of other pyranosyl nucleosides, such as

\* 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 53589 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

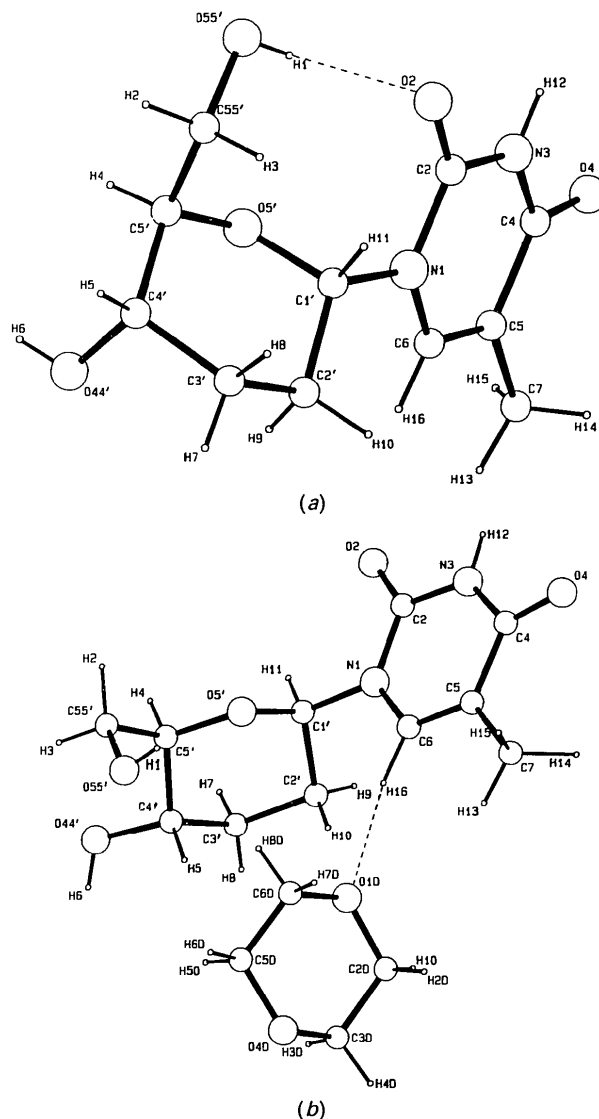


Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) plot of the title compounds with atomic numbering scheme. Dashed lines indicate hydrogen bonds.

Table 2. Atomic coordinates and equivalent isotropic temperature factors (Å<sup>2</sup> × 10<sup>4</sup>) with e.s.d.'s in parentheses
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	<i>U</i> <sub>eq</sub>
(I)				
N(1)	0.0582 (4)	0.5449 (1)	0.81687 (9)	338 (4)
C(2)	0.0772 (5)	0.4429 (2)	0.8348 (1)	377 (5)
O(2)	0.2226 (4)	0.3837 (1)	0.80233 (9)	531 (5)
N(3)	-0.0804 (5)	0.4137 (1)	0.89128 (9)	414 (5)
C(4)	-0.2620 (6)	0.4724 (2)	0.9292 (1)	401 (6)
O(4)	-0.4026 (5)	0.4353 (1)	0.97645 (9)	640 (5)
C(5)	-0.2688 (5)	0.5793 (2)	0.9092 (1)	372 (5)
C(6)	-0.1133 (5)	0.6092 (2)	0.8539 (1)	343 (5)
C(7)	-0.4487 (6)	0.6492 (2)	0.9510 (1)	505 (6)
C(1')	0.2039 (5)	0.5728 (2)	0.7513 (1)	319 (5)
C(2')	0.2537 (5)	0.6840 (2)	0.7380 (1)	365 (5)
C(3')	0.4238 (5)	0.6885 (2)	0.6690 (1)	398 (5)
C(4')	0.2840 (5)	0.6355 (2)	0.6067 (1)	350 (5)
C(5')	0.1794 (5)	0.5301 (2)	0.6269 (1)	331 (5)
O(5')	0.0412 (3)	0.5318 (1)	0.69538 (7)	313 (4)
O(44')	0.0646 (4)	0.6993 (1)	0.58308 (8)	423 (4)
C(55')	0.4012 (6)	0.4486 (2)	0.6260 (1)	451 (6)
O(55')	0.3011 (5)	0.3549 (1)	0.65199 (9)	578 (5)
(II)				
N(1)	0.8512 (1)	1.0004 (4)	0.6385 (2)	366 (8)
C(2)	0.9111 (1)	0.9920 (5)	0.5838 (2)	362 (6)
O(2)	0.9812 (1)	0.9877 (4)	0.6228 (1)	499 (5)
N(3)	0.8850 (1)	0.9881 (4)	0.4801 (2)	424 (5)
C(4)	0.8084 (2)	0.9877 (5)	0.4271 (2)	413 (6)
O(4)	0.7950 (1)	0.9796 (5)	0.3342 (2)	610 (6)
C(5)	0.7486 (2)	0.9934 (5)	0.4896 (2)	416 (6)
C(6)	0.7727 (2)	0.9978 (5)	0.5904 (2)	414 (6)
C(7)	0.6631 (2)	0.9969 (7)	0.4379 (3)	595 (9)
C(1')	0.8718 (1)	0.9951 (5)	0.7501 (2)	371 (6)
C(2')	0.8338 (2)	1.1446 (4)	0.7984 (2)	490 (8)
C(3')	0.8504 (2)	1.1178 (5)	0.9136 (2)	503 (8)
C(4')	0.8255 (2)	0.9373 (4)	0.9409 (2)	446 (8)
C(5')	0.8651 (2)	0.8010 (4)	0.8857 (2)	378 (6)
O(5')	0.8467 (1)	0.83 (†)	0.7782 (1)	376 (4)
O(44')	0.8487 (2)	0.9033 (4)	1.0464 (2)	658 (8)
C(55')	0.8425 (2)	0.6139 (5)	0.9025 (2)	523 (9)
O(55')	0.7617 (2)	0.5802 (4)	0.8661 (2)	599 (6)
O(1D)	0.6274 (2)	1.0003 (7)	0.7053 (3)	1188 (11)
C(2D)	0.5709 (3)	1.1222 (9)	0.7017 (5)	1268 (25)
C(3D)	0.5266 (3)	1.1149 (8)	0.7810 (5)	1052 (13)
O(4D)	0.5008 (2)	0.9441 (8)	0.7949 (4)	1420 (13)
C(5D)	0.5623 (4)	0.8265 (9)	0.8052 (6)	1235 (25)
C(6D)	0.6035 (3)	0.8357 (9)	0.7257 (6)	1320 (25)

(†) Origin-defining.

in the antibiotic amicitin (Smith & Sundaralingam, 1981) and cytosamine triacetate (Sygusch, Brisse & Hannessian, 1974), where a comparable shortening of 0.022 (8) and 0.020 (8) Å, respectively, exists. The sugar-base C(1')—N(1) glycosyl bond distances of 1.463 (3) (I) and 1.469 (3) Å (II) are shortened compared to the mean value of 1.491 (4) Å observed in the corresponding pyrimidine furanosyl nucleosides (Lin, Sundaralingam & Arora, 1971).

Using the method of Cremer & Pople (1975), we calculated as phase angles  $\varphi_2 = 21$  (1) (I) and 36 (18)<sup>o</sup> (II) and  $\theta_2 = 12.7$  (2) (I) and 178.9<sup>o</sup> (4) (II), with total puckering amplitudes  $Q = 0.571$  (1) (I) and 0.564 (4) Å (II) for the sequences C(1')—C(2')—C(3')—C(4')—C(5')—O(5'). These puckering parameters describe for both molecules a slightly distorted

Table 3. Bond lengths (Å), bond angles (°) and selected torsion angles (°) with e.s.d.'s in parentheses

	(I)	(II)
N(1)—C(2)	1.389 (3)	1.378 (3)
N(1)—C(6)	1.377 (3)	1.383 (3)
N(1)—C(1')	1.463 (3)	1.469 (3)
C(2)—O(2)	1.216 (3)	1.219 (3)
C(2)—N(3)	1.361 (4)	1.376 (3)
N(3)—C(4)	1.372 (3)	1.373 (3)
C(4)—O(4)	1.220 (4)	1.223 (3)
C(4)—C(5)	1.459 (3)	1.448 (4)
C(5)—C(6)	1.340 (3)	1.335 (4)
C(5)—C(7)	1.493 (4)	1.502 (4)
C(1')—C(2')	1.506 (3)	1.524 (5)
C(1')—O(5')	1.419 (3)	1.408 (4)
C(2')—C(3')	1.534 (3)	1.529 (4)
C(3')—C(4')	1.519 (3)	1.512 (5)
C(4')—O(44')	1.430 (3)	1.417 (3)
C(4')—C(5')	1.527 (3)	1.515 (4)
C(5')—O(5')	1.445 (2)	1.432 (3)
C(5')—C(55')	1.524 (3)	1.512 (5)
C(55')—O(55')	1.414 (3)	1.408 (4)
O(1D)—C(2D)		1.343 (8)
O(1D)—C(6D)		1.370 (9)
C(2D)—C(3D)		1.423 (9)
C(3D)—O(4D)		1.405 (9)
O(4D)—C(5D)		1.377 (8)
C(5D)—C(6D)		1.39 (1)
N(1)—C(2)—O(2)	122.7 (3)	123.7 (2)
N(1)—C(2)—N(3)	115.0 (2)	114.0 (2)
N(1)—C(6)—C(5)	123.3 (2)	123.9 (3)
N(1)—C(1')—C(2')	117.5 (2)	111.9 (2)
N(1)—C(1')—O(5')	104.5 (2)	105.7 (2)
C(2)—N(1)—C(6)	121.0 (2)	121.2 (2)
C(2)—N(1)—C(1')	114.5 (2)	118.8 (2)
C(2)—N(3)—C(4)	127.2 (2)	128.1 (2)
O(2)—C(2)—N(3)	122.3 (2)	122.3 (2)
N(3)—C(4)—O(4)	120.7 (3)	120.0 (3)
N(3)—C(4)—C(5)	115.3 (2)	114.9 (2)
C(4)—C(5)—C(6)	117.9 (3)	117.9 (2)
C(4)—C(5)—C(7)	118.4 (3)	118.6 (2)
O(4)—C(4)—C(5)	124.1 (2)	125.0 (2)
C(6)—N(1)—C(1')	124.2 (2)	119.8 (2)
C(6)—C(5)—C(7)	123.6 (2)	123.4 (3)
C(1')—C(2')—C(3')	105.3 (2)	108.4 (3)
C(1')—O(5')—C(5')	113.5 (2)	112.9 (2)
C(2')—C(1')—O(5')	109.8 (2)	112.3 (2)
C(2')—C(3')—C(4')	112.7 (2)	111.1 (3)
C(3')—C(4')—C(5')	112.2 (2)	109.5 (3)
C(3')—C(4')—O(44')	107.5 (2)	111.7 (2)
C(4')—C(5')—O(5')	111.2 (2)	110.6 (2)
C(4')—C(5')—C(55')	113.7 (2)	115.2 (3)
C(5')—C(55')—O(55')	111.7 (2)	112.8 (3)
O(44')—C(4')—C(5')	111.2 (2)	107.1 (2)
C(55')—C(5')—O(5')	110.5 (2)	106.5 (2)
O(1D)—C(2D)—C(3D)		115.9 (6)
O(1D)—C(6D)—C(5D)		114.6 (6)
C(2D)—O(1D)—C(6D)		113.7 (5)
C(2D)—C(3D)—O(4D)		111.4 (5)
C(3D)—O(4D)—C(5D)		111.3 (4)
O(4D)—C(5D)—C(6D)		112.8 (6)
(2')—C(1')—O(5')—C(5')	66.7 (2)	-59.8 (3)
O(5')—C(1')—C(2')—C(3')	-64.4 (2)	55.0 (4)
C(1')—C(2')—C(3')—C(4')	56.2 (2)	-53.2 (4)
C(2')—C(3')—C(4')—O(44')	74.4 (2)	173.3 (3)
C(2')—C(3')—C(4')—C(5')	-48.2 (3)	54.8 (4)
C(3')—C(4')—C(5')—C(55')	-80.7 (3)	-177.4 (3)
C(3')—C(4')—C(5')—O(5')	44.8 (3)	-56.6 (3)
C(3')—C(4')—O(44')—H(6)	179 (2)	71 (4)
O(44')—C(4')—C(5')—C(55')	158.8 (2)	61.2 (4)
O(44')—C(4')—C(5')—O(5')	-175.7 (2)	-177.9 (2)
C(5')—C(4')—O(44')—H(6)	-57 (2)	-169 (4)
C(4')—C(5')—O(5')—C(1')	-54.8 (2)	59.9 (3)
C(55')—C(5')—O(5')—C(1')	72.5 (2)	-174.2 (2)
C(4')—C(5')—C(55')—O(55')	174.1 (2)	63.0 (4)
O(5')—C(5')—C(55')—O(55')	48.2 (3)	-60.0 (4)
C(5')—C(55')—O(55')—H(1)	296 (2)	74 (4)

Table 4. Geometry of intra- and intermolecular hydrogen bonds ( $\text{\AA}$ ,  $^\circ$ ) with e.s.d.'s in parentheses

(I)			
$X-H\cdots Y$	$d(H\cdots Y)$	$d(X\cdots Y)$	$X-H\cdots Y$
$O(55')-H(1)\cdots O(2)$	2.10 (2)	2.859 (3)	171 (3)
$C(5')-H(4)\cdots O(4')$	2.43 (2)	3.151 (3)	134 (2)
$O(44')-H(6)\cdots O(4)$	2.04 (2)	2.781 (3)	155 (3)
$C(3')-H(7)\cdots O(2)''$	2.42 (3)	3.143 (3)	133 (2)
$C(6)-H(16)\cdots O(55')'''$	2.51 (2)	3.368 (3)	152 (2)
$C(7)-H(13)\cdots O(55')'''$	2.49 (2)	3.401 (3)	158 (2)
$N(3)-H(12)\cdots O(44')''$	2.03 (3)	2.868 (3)	171 (2)
Symmetry code: (i) $-x - \frac{1}{2}, 1 - y, z - \frac{1}{2}$ ; (ii) $1 - x, y + \frac{1}{2}, \frac{3}{2} - z$ ; (iii) $-x, y + \frac{1}{2}, \frac{3}{2} - z$ ; (iv) $-x, y - \frac{1}{2}, \frac{3}{2} - z$ .			
(II)			
$X-H\cdots Y$	$d(H\cdots Y)$	$d(X\cdots Y)$	$X-H\cdots Y$
$C(6)-H(16)\cdots O(1D)$	2.14 (4)	3.182 (5)	171 (3)
$O(55')-H(1)\cdots O(4')$	2.15 (4)	2.782 (3)	148 (4)
$O(44')-H(6)\cdots O(55')''$	1.97 (5)	2.773 (4)	160 (4)
$N(3)-H(12)\cdots O(2)'''$	2.04 (4)	2.906 (3)	176 (3)
Symmetry code: (i) $\frac{3}{2} - x, y - \frac{1}{2}, 1 - z$ ; (ii) $\frac{3}{2} - x, y + \frac{1}{2}, 2 - z$ ; (iii) $2 - x, y, 1 - z$ .			

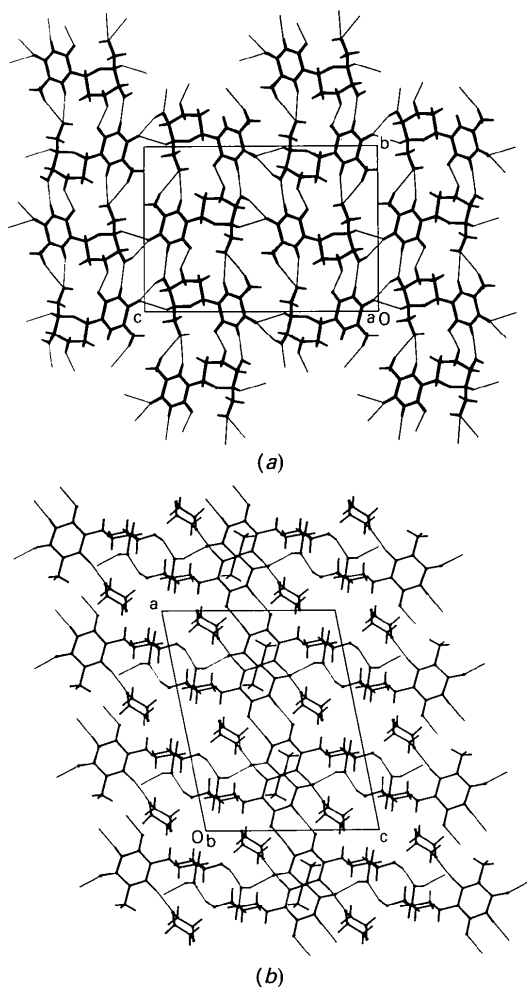


Fig. 2. PLUTO (Motherwell &amp; Clegg, 1978) plot of the crystal (a) along a (I) and (b) along b (II) showing the packing. Thin lines indicate hydrogen bonds.

chair conformation, with the total puckering amplitudes  $Q$  only slightly lower than for an ideal cyclohexane chair (0.63  $\text{\AA}$ ; Cremer & Pople, 1975) and slightly flattened at the C(4') (I) and C(1') (II) apex. Of the three sugar substituents in compound (I), only the heterocyclic nucleobase is placed equatorially with respect to the ring, while both C(55') and O(44') are found to be in an axial orientation. This is in contrast with (II), where all the substituents are positioned equatorially.

The relative orientation of the base with respect to the sugar ring is given by the  $N$ -glycosidic torsion angle  $\chi$  [ $O(5')-C(1')-N(1)-C(2)$ ], which is  $73.0 (2)^\circ (+sc)$  for (I) and  $251.4 (3)^\circ (-ac)$  for (II).

For the dioxane ring present in the crystal structure of the  $\beta$  enantiomer, we calculated, using the method of Cremer & Pople (1975), a phase angle  $\varphi_2 = 12 (7)^\circ$  and  $\theta_2 = 172.2 (6)^\circ$ , with a total puckering amplitude of  $Q = 0.451 (6) \text{\AA}$  for the sequence  $O(1D)-C(2D)-C(3D)-O(4D)-C(5D)-C(6D)$ . Considering that this amplitude is significantly smaller than the 0.562 (1)  $\text{\AA}$  from the low-temperature study of dioxane (Buschmann, Müller & Luger, 1986), and considering the extremely short cyclic bond distances, the large thermal parameters of the dioxane atoms and the minimum and maximum residual electron density ( $-0.27$  and  $+0.37 e \text{\AA}^{-3}$ ) in the environment of this dioxane molecule, we suspect the ring to be partially disordered.

Table 4 summarizes all the intra- and intermolecular hydrogen bonds. A PLUTO (Motherwell & Clegg, 1978) plot of both crystal packings is shown in Fig. 2. In both crystals the hydrogen bonds determine the packing along all the crystallographic axes.

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### Three Stereoisomeric Methyl 8-Bromo-2,3-diphenyl-2,3,3a,9b-tetrahydro-1H,4H-[1]benzopyrano[4,3-b]pyrrole-2-carboxylates

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**Abstract.** C<sub>25</sub>H<sub>22</sub>BrNO<sub>3</sub>, *M<sub>r</sub>* = 464.4, Cu Kα, λ = 1.5418 Å, μ = 2.88 mm<sup>-1</sup>, *T* = 298 K. (A) Monoclinic, *P*2<sub>1</sub>/*c*, *a* = 9.848 (2), *b* = 12.935 (2), *c* = 16.549 (2) Å, β = 92.81 (1)°, *V* = 2105.5 (5) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.456, *D<sub>x</sub>* = 1.464 Mg m<sup>-3</sup>, *F*(000) = 952, *R* = 0.0363 for 2880 observed reflections. (B) Monoclinic, *C*2/*c*, *a* = 48.06 (1), *b* = 6.159 (1), *c* = 14.829 (3) Å, β = 103.76 (2)°, *V* = 4263 (2) Å<sup>3</sup>, *Z* = 8, *D<sub>m</sub>* = 1.452, *D<sub>x</sub>* = 1.446 Mg m<sup>-3</sup>, *F*(000) = 1904, *R* = 0.0426 for 2834 observed reflections. (C) Monoclinic, *P*2<sub>1</sub>/*c*, *a* = 11.664 (2), *b* = 22.979 (3), *c* = 15.985 (3) Å, β = 101.37 (1)°, *V* = 4200 (1) Å<sup>3</sup>, *Z* = 8, *D<sub>m</sub>* = 1.477, *D<sub>x</sub>* = 1.468 Mg m<sup>-3</sup>, *F*(000) = 1904, *R* = 0.0436 for 5176 observed reflections. These isomers consist of three pairs of racemic and configurational isomers which are caused by the asymmetric C atoms in the pyrrole rings, and isomer (C) consists of two pairs of conformational isomers caused by torsions between the benzopyrano and pyrrole rings. Isomers (A) and (C) have intramolecular O⋯HN hydrogen bonds between the carbonyl and pyrrole moieties.

**Introduction.** During the course of studies on the intramolecular 1,3-dipolar cycloaddition of imines of

glycine esters to carbon–carbon multiple bonds, methyl 2-[2-(cinnamyloxy)benzylideneamino]-2-phenylacetates were found to give thermally three stereoisomeric cycloadducts (Tuge, Ueno & Ueda, 1981) as shown in (I). The X-ray analyses were carried out to reveal the conformations of isomeric cycloadducts (A), (B) and (C) in order to know the stereochemical course in the intramolecular cycloaddition of the bromine-substituted imine.

