Only eight of the ten available H atoms are used in definite H bonding (*cf.* Fig. 1); there is a ninth possible H bond shown, N(10)···N(7), but this is 3·316 (10) Å, and probably outside the range. As the electron density around the N atoms in the difference map was somewhat diffuse, it is not possible to be absolutely certain as to the H-atom positions, so confirmation of the H-bonding scheme will need to await a neutron analysis.

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The Structure of 3,5-Di-O-benzoyl-1,2-dideoxy-1-phenyl-β-D-ribofuranose, C25H22O5

BY J. GUNNING AND S. NEIDLE*

Cancer Research Campaign Biomolecular Structure Research Group, Department of Biophysics, King's College, 26–29 Drury Lane, London WC2B 5RL, England

T. A. MILLICAN, M. A. W. EATON AND G. A. MOCK

Celltech Ltd, 244–250 Bath Road, Slough SL1 4DY, Berkshire, England

AND J. MANN

Department of Chemistry, University of Reading, Reading RG6 2AD, Berkshire, England

Abstract. $M_r = 402·4$, orthorhombic, $P2_12_12_1$, $a = 4·946 (1)$, $b = 15·887 (2)$, $c = 26·555 (2)$ Å, $V = 2086·7 (5)$ Å^3, $Z = 4$, $D_x = 1·28$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 6·868$ cm^{-1}, $F(000) = 848$, $T = 293$ K, final $R = 0·054$ for 648 observed reflections. The molecule is propeller shaped. The benzoyl groups act as protecting groups and the phenyl group is a base substitute. The crystal structure does not involve any intermolecular stacking interactions between the phenyl groups. The molecules pack in typical herring-bone-like arrays. The sugar has a β-D configuration with C(2')-*endo*–C(3')-*exo* pucker ($^2T_3$), pseudorotation angle $P = 172 (2)°$, degree of pucker $\tau_m = 39 (2)°$.

Introduction. This molecule was synthesized as a protected base analogue for eventual insertion into an oligonucleotide strand in order to investigate its effects on DNA duplex stability (Millican, Mock, Eaton, Patel, Chauncey, Mann, Gunning, Cutbush & Neidle, 1984).

This forms an initial part of a series of experiments to design a 'universal' base, which would obviate the necessity for synthesizing multiple gene probes in cases where there are ambiguities in the genetic code.

Experimental. Recrystallization from diethyl ether as colourless needles, Enraf–Nonius CAD-4 diffractometer, crystal fragment $0·2 \times 0·1 \times 0·05$ mm, Ni-filtered Cu $K\alpha$ radiation. Unit cell from θ values of 25 reflections, $\omega/2\theta$ mode, max. scan time 120 s, 1424 measured reflections, unique set of 648 with $I > 2\sigma(I)$, $1·5 < \theta < 50°$, index range h 0/4, k 0/15, l 0/25; Lp corrections. Structure solved by direct methods with *MULTAN*80 (Main *et al.*, 1980); H in calculated positions and not refined; common B of 5·0 Å^2 assigned. Full-matrix least-squares refinement (with Enraf–Nonius *SDP* package; Frenz, 1978); anisotropic temperature factors only for O atoms, due to small number of observations; isotropic temperature factors for all other non-hydrogen atoms, $R = 0·054$, $wR = 0·055$ with $w = 1/\sigma^2(F)$, max. $\Delta/\sigma = 0·01$, max. and min. densities in final difference synthesis 0·3 and $-0·2$ e Å^{-3}, minimization of $\sum w(|F_o| - |F_c|)^2$. Atom

* To whom correspondence should be addressed. Present address: Institute of Cancer Research, Clifton Avenue, Sutton, Surrey SM2 5PX, England.

Table 1. *Fractional atomic coordinates and temperature factors for non-hydrogen atoms with e.s.d.'s in parentheses*

Starred atoms were refined isotropically. For anisotropically refined atoms $B_{eq} = 8\pi^2(U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	B_{eq}/B_{iso}(Å^2)
O(4')	0.656 (1)	0.7032 (4)	0.2793 (2)	4.0 (2)
O(3')	0.605 (2)	0.5676 (4)	0.1999 (2)	4.5 (2)
O(3'B)	0.595 (2)	0.6243 (4)	0.1227 (2)	6.0 (2)
O(5')	0.293 (2)	0.7978 (4)	0.1760 (2)	5.4 (2)
O(5'B)	0.008 (2)	0.8988 (5)	0.1982 (2)	8.0 (3)
C(1')	0.561 (2)	0.6252 (6)	0.3028 (3)	4.3 (3)*
C(2')	0.319 (2)	0.5998 (6)	0.2686 (3)	4.3 (3)*
C(3')	0.414 (2)	0.6288 (6)	0.2177 (3)	3.9 (3)*
C(3'B)	0.677 (2)	0.5723 (7)	0.1512 (3)	4.5 (3)*
C(4')	0.556 (2)	0.7112 (6)	0.2291 (3)	3.5 (2)*
C(5'B)	0.111 (2)	0.8580 (6)	0.1662 (4)	4.7 (3)*
C(5')	0.367 (2)	0.7856 (6)	0.2281 (3)	5.0 (3)*
C(1B1)	0.496 (2)	0.6439 (6)	0.3563 (3)	3.6 (2)*
C(1B2)	0.881 (2)	0.5079 (6)	0.1380 (3)	3.7 (3)*
C(1B3)	0.058 (2)	0.8642 (6)	0.1111 (3)	4.1 (3)*
C(2B1)	0.290 (2)	0.6988 (6)	0.3702 (3)	4.8 (3)*
C(2B2)	0.971 (2)	0.4477 (6)	0.1726 (3)	3.5 (2)*
C(2B3)	0.203 (3)	0.8176 (7)	0.0760 (3)	5.1 (3)*
C(3B1)	0.240 (3)	0.7176 (8)	0.4204 (4)	6.3 (3)*
C(3B2)	1.163 (2)	0.3889 (6)	0.1580 (4)	4.8 (3)*
C(3B3)	0.151 (3)	0.8278 (8)	0.0250 (4)	6.6 (3)*
C(4B1)	0.393 (3)	0.6792 (7)	0.4568 (4)	5.7 (3)*
C(4B2)	1.269 (2)	0.3911 (7)	0.1104 (4)	5.3 (3)*
C(4B3)	−0.042 (3)	0.8818 (7)	0.0098 (4)	6.0 (3)*
C(5B1)	0.586 (3)	0.6234 (7)	0.4450 (4)	6.6 (3)*
C(5B2)	1.188 (2)	0.4494 (7)	0.0773 (4)	5.2 (3)*
C(5B3)	−0.190 (3)	0.9287 (7)	0.0438 (4)	5.8 (3)*
C(6B1)	0.642 (3)	0.6043 (7)	0.3940 (4)	5.6 (3)*
C(6B2)	0.991 (2)	0.5075 (6)	0.0902 (3)	4.3 (3)*
C(6B3)	−0.135 (2)	0.9198 (7)	0.0948 (4)	5.5 (3)*

Table 2. *Bond distances (Å) and angles (°) with e.s.d.'s in parentheses*

O(4')	C(1')	1.465 (11)	C(3B1)	C(4B1)	1.370 (16)
O(3')	C(3')	1.435 (12)	C(3B2)	C(4B2)	1.369 (14)
O(3'B)	C(3'B)	1.192 (12)	C(3B3)	C(4B3)	1.344 (18)
O(5')	C(5'B)	1.340 (13)	C(4B1)	C(5B1)	1.340 (17)
O(5'B)	C(5'B)	1.184 (12)	C(4B2)	C(5B2)	1.338 (14)
C(1')	C(2')	1.555 (15)	C(4B3)	C(5B3)	1.381 (16)
C(2')	C(3')	1.503 (13)	C(5B1)	C(6B1)	1.416 (14)
C(3')	C(4')	1.515 (13)	C(5B2)	C(6B2)	1.386 (15)
C(3'B)	C(1B2)	1.478 (15)	C(5B3)	C(6B3)	1.389 (14)
C(4')	C(5')	1.507 (14)	O(4')	C(4')	1.427 (10)
C(5'B)	C(1B3)	1.490 (13)	O(3')	C(3'B)	1.344 (11)
C(1B1)	C(2B1)	1.392 (15)	O(5')	C(5')	1.443 (11)
C(1B2)	C(2B2)	1.398 (13)	C(1')	C(1B1)	1.487 (12)
C(1B3)	C(2B3)	1.390 (14)	C(1B1)	C(6B1)	1.386 (14)
C(2B1)	C(3B1)	1.387 (13)	C(1B2)	C(6B2)	1.381 (13)
C(2B2)	C(3B2)	1.387 (15)	C(1B3)	C(6B3)	1.370 (15)
C(2B3)	C(3B3)	1.388 (14)			

O(4')	C(1')	C(2')	102.5 (7)	C(1B3)	C(2B3)	C(3B3)	119.8 (11)
O(4')	C(4')	C(3')	105.7 (7)	C(1B3)	C(6B3)	C(5B3)	120.8 (10)
O(3')	C(3')	C(2')	107.1 (7)	C(2B1)	C(1B1)	C(6B1)	118.3 (8)
O(3')	C(3'B)	O(3'B)	123.9 (10)	C(2B1)	C(3B1)	C(4B1)	118.9 (11)
O(3'B)	C(3'B)	C(1B2)	124.2 (9)	C(2B2)	C(1B2)	C(6B2)	118.4 (9)
O(5')	C(5'B)	O(5'B)	122.6 (9)	C(2B2)	C(3B2)	C(4B2)	120.2 (9)
O(5')	C(5')	C(4')	106.3 (7)	C(2B3)	C(1B3)	C(6B3)	119.3 (9)
O(5'B)	C(5'B)	C(1B3)	126.4 (10)	C(2B3)	C(3B3)	C(4B3)	119.9 (11)
C(1')	O(4')	C(4')	111.2 (7)	C(3B1)	C(4B1)	C(5B1)	121.6 (10)
C(1')	C(2')	C(3')	101.8 (8)	C(3B2)	C(4B2)	C(5B2)	120.6 (10)
C(1')	C(1B1)	C(2B1)	122.6 (8)	C(3B3)	C(4B3)	C(5B3)	121.5 (10)
C(2')	C(1')	C(1B1)	116.2 (9)	C(4B1)	C(5B1)	C(6B1)	120.2 (10)
C(2')	C(3')	C(4')	103.2 (7)	C(4B2)	C(5B2)	C(6B2)	120.6 (9)
C(3')	O(3')	C(3'B)	117.0 (7)	C(4B3)	C(5B3)	C(6B3)	118.6 (11)
C(3')	C(4')	C(5')	112.8 (9)	O(4')	C(1')	C(1B1)	107.9 (7)
C(3'B)	C(1B2)	C(2B2)	122.2 (8)	O(4')	C(4')	C(5')	107.5 (7)
C(5'B)	O(5')	C(5')	117.0 (7)	O(3')	C(3')	C(4')	110.2 (8)
C(5'B)	C(1B3)	C(2B3)	122.3 (9)	O(3')	C(3'B)	C(1B2)	111.8 (8)
C(1B1)	C(2B1)	C(3B1)	121.3 (9)	O(5')	C(5'B)	C(1B3)	110.8 (8)
C(1B1)	C(6B1)	C(5B1)	119.5 (10)	C(1')	C(1B1)	C(6B1)	119.1 (9)
C(1B2)	C(2B2)	C(3B2)	119.6 (8)	C(3'B)	C(1B2)	C(6B2)	119.3 (8)
C(1B2)	C(6B2)	C(5B2)	120.5 (9)	C(5'B)	C(1B3)	C(6B3)	118.3 (9)

scattering factors from *International Tables for X-ray Crystallography* (1974). Figures were drawn with *PLUTO* (Motherwell & Clegg, 1978).

Discussion. The final atomic coordinates are given in Table 1* and bond lengths and angles in Table 2. The packing of the molecules within the unit cell is shown in Fig. 1. The molecules pack so that the aromatic rings do not stack above each other but at an angle with the fewest possible intermolecular contacts. The crystal lattice is formed by herring-bone-like arrays typical of those found for other apolar aromatic cyclic compounds (Bugg, Thomas, Sundaralingam & Rao, 1971).

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39885 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
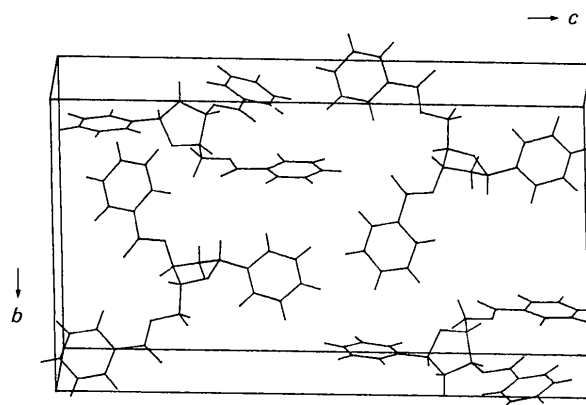

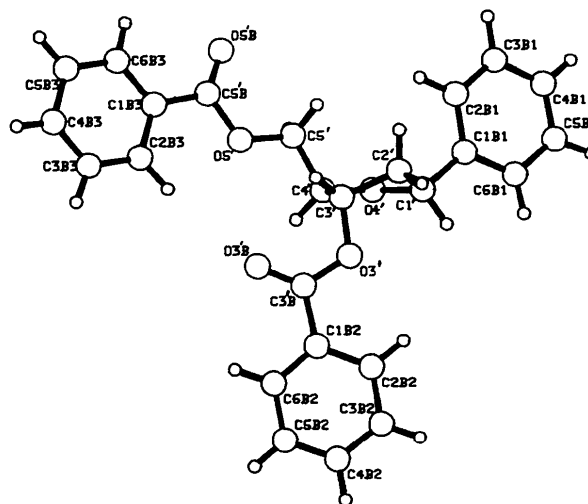Fig. 1. The molecular packing within the unit cell viewed down **a**.

Fig. 2. The molecular structure showing the numbering scheme used.

Table 3. *Details of the sugar pucker in terms of torsion angles and atomic displacements*

Torsion angles in degrees (average e.s.d. = 1°)

$\tau 0$	−18	$\|C(4')-O(4')-C(1')-C(2')\|$
$\tau 1$	34	$\|O(4')-C(1')-C(2')-C(3')\|$
$\tau 2$	−39	$\|C(1')-C(2')-C(3')-C(4')\|$
$\tau 3$	29	$\|C(2')-C(3')-C(4')-C(4')\|$
$\tau 4$	−6	$\|C(3')-C(4')-O(4')-C(1')\|$

Displacement from $C(4')-O(4')-C(1')$ plane in Å (average e.s.d. = 0·03 Å)

C(2')	0·46
O(3')	−0·17
C(5')	1·31

The molecular structure found (Fig. 2) confirms the chemical and spectral assignments of a $β$-D-ribose sugar. The molecule adopts a propeller shape with the benzoyl substituents attached to the hydroxyl positions of the deoxyribose sugar; phenyl rings $B2$ and $B3$ are protecting groups and $B1$ a substitute for a base. Since the $B2$ phenyl ring is symmetric, it is not possible to define a glycosidic angle as in nucleosides and nucleotides. The ribofuranose ring is in the unsymmetric twist $^2T_3$ conformation, which can also be defined in terms of the $C(2')$-*endo*–$C(3')$-*exo* sugar pucker. The pseudorotation angle (Altona & Sundaralingam, 1972) P is 172 (2)° and maximum degree of sugar pucker τ_m is 39 (2)°. The sugar-ring torsion angles are given in Table 3.

Biophysical studies (Millican *et al.*, 1984) have shown that the insertion of this deoxyribose base analogue into a pentadecanucleotide destabilizes base stacking. This may be related to the lack of stacking shown by the pseudo-base phenyl ring in the present structure.

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Supinine, C₁₅H₂₅NO₄, and Heleurine, C₁₆H₂₇NO₄, Pyrrolizidine Alkaloids

BY M. F. MACKAY, P. MITRPRACHACHON AND P. J. OLIVER

Department of Physical Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

AND C. C. J. CULVENOR

Division of Animal Health, CSIRO, Parkville, Victoria 3052, Australia

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Abstract. Orthorhombic, $P2_12_12_1$, $Z = 4$, $\lambda(\text{Cu } K\alpha)$ = 1·5418 Å, $T = 290$ (1) K. Supinine: $M_r = 283\cdot4$, $a = 10\cdot068$ (1), $b = 11\cdot644$ (1), $c = 13\cdot086$ (1) Å, U = 1534·1 (2) Å³, $D_m(\text{flotation}) = 1\cdot23$ (1), $D_x =$ 1·230 Mg m⁻³, $F(000) = 616$, $\mu(\text{Cu } K\alpha) = 0\cdot64$ mm⁻¹. Heleurine: $M_r = 297\cdot4$, $a = 9\cdot269$ (1), $b = 11\cdot175$ (1), $c = 16\cdot345$ (2) Å, $U = $'1693·0 (3) Å³, $D_m(\text{flotation}) = 1\cdot18$ (1), $D_x = 1\cdot167$ Mg m⁻³, $F(000) = 648$, $\mu(\text{Cu } K\alpha) = 0\cdot60$ mm⁻¹. Full-matrix least-squares refinement converged at R values of 0·041 and 0·048 for 1411 and 1367 reflections of supinine and heleurine respectively. The absolute molecular structures have been assigned by comparison with that of the amino-alcohol, supinidine. Both alkaloid molecules adopt similar extended conformations which differ from that of intermedine, a retronecine alkaloid also containing the trachelanthic acid moiety, by an approximate twofold rotation about the C(1)–C(9) bond. Consequently, in supinine and heleurine the carbonyl group is antiparallel with the C(8)–H(8) bond whereas in intermedine it is synparallel.

Introduction. The two alkaloids, monoesters of the amino-alcohol supinidine (I), have been isolated from *Heliotropium europaeum* L. (Culvenor, 1954), supinine being only a minor product; the latter was however isolated from *H. supinum* L. as one of three major bases (Crowley & Culvenor, 1959). As in the retronecine monoester, intermedine, the acid moiety in supinine (II) is (+)-trachelanthic acid; the acid moiety in heleurine (III) is (−)-heliotric acid as in the heliotridine monoester, heliotrine (Bull, Culvenor &