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Conformation of the Monomeric Unit in AP Sites in Nucleic Acids: Structure of Methyl 2-Deoxy-3,5-di-*O*-*p*-nitrobenzoyl-β-D-ribofuranoside

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Abstract

The structure of the title compound, $C_{20}H_{18}N_2O_{10}$, was determined by X-ray diffraction. $M_r = 446{\cdot}37$, orthorhombic, $P2_12_12_1$, $a = 21{\cdot}103(3)$, $b = 21{\cdot}860(3)$, $c = 4{\cdot}4096(14)$ Å, $V = 2034{\cdot}2(8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}46$ Mg m^{-3}, Cu $K\alpha$ radiation (graphite-monochromized, $\lambda = 1{\cdot}54180$ Å), μ(Cu $K\alpha$) = $1{\cdot}033$ mm^{-1}, $F(000) = 928$, $T = 290$ K, final conventional R factor = 0·035, $wR = 0{\cdot}040$ for 2454 reflections and 343 variables. The structure was solved by combined Patterson and direct methods. The configuration of the carbohydrate at C(1) is β. The conformation of the five-membered sugar ring is best described as an intermediate between ${}_0^1T$ and ${}^1E$; the pseudorotational parameters for this ring are $P = -68{\cdot}3°$, $\varphi_m = 33{\cdot}7°$. The variability of C–O bond lengths in the anomeric moiety C(4)–O(4)–C(1)–O(1)–C(1′) is discussed in terms of the anomeric effect. The conformation of the *endo* anomeric bond O(4)–C(1), represented by the torsion angle C(4)–O(4)–C(1)–O(1) (−84·2°), and that of the *exo* anomeric bond C(1)–O(1), represented by the torsion angle O(4)–C(1)–O(1)–C(1′) (−68·2°), can be described as near-*gauche* and *gauche* respectively.

Introduction

The present work is the first part of a series of conformational studies on complementary *d*-oligonucleotides in which a nucleotide residue has been replaced by methyl 2-deoxy-α- (or -β-) D-ribofuranoside-5-phosphate. Double helical complexes formed from these base-deleted oligonucleotides may form convenient models for the investigation of the conformational features and recognition mechanism by proteins of apurinic or apyrimidinic (AP) sites in nucleic acids.

An examination of the literature reveals that the only accurate data available concern crystal structures of acetylated β-D-glycofuranoses. In the present paper we describe the first crystal structure of a methyl 2-deoxy-β-D-ribofuranoside.

In order to gain a fundamental insight into the conformational behaviour of base-deleted oligonucleotides, a thorough knowledge of the structural characteristics of the monomeric base-deleted sugar unit is a prerequisite.

Experimental

The title compound was prepared according to the procedure of Ness, MacDonald & Fletcher (1961). Light-yellow crystals, suitable for X-ray analysis, were obtained by evaporation from a dichloromethane solution.

Crystal 0·06 × 0·10 × 0·33 mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromized Cu $K\alpha$ radiation, ω–2θ scan, scan angle = 1°, lattice parameters from 22 reflections in the range θ = 14·7–28·3°, 9668 intensities measured with $\theta_{max} = 70°$ in the quadrant $-25 \le h \le 25$, $0 \le k \le 26$, $0 \le l \le 6$. The intensity of the primary beam was checked by monitoring three standard reflections every 30 min of X-ray exposure time; final drift corrections were between 1·00 and 1·04. A profile analysis (Lehman & Larsen, 1974; Grant & Gabe, 1978) was performed on all reflections. An empirical absorption correction using ψ scans (North, Phillips & Mathews, 1968) was applied (minimum transmission 97%, average transmission 98%). Laue symmetry equivalent reflections were averaged, $R_{int} = 0{\cdot}019$, resulting in 3866 unique reflections of which 2454 were observed with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied and the data were reduced to F_{obs} values.

Several direct-method E maps (*MULTAN*, Main *et al.*, 1980) did not lead to any chemically reasonable

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structure. Three different *MULTAN* phase sets were used as inputs to a new method based upon the convolution of poorly phased *E* maps (Bruins Slot & Beurskens, 1987*a*) and led to the identification of a well-defined *p*-nitrobenzoyl fragment. The orientation of this fragment was confirmed by the orientation search program *ORIENT* (Strumpel, Beurskens, Beurskens, Haltiwanger & Bosman, 1983). The position of this fragment was found using *PATSEE* (Egert, 1984) and, independently, by translation functions based on the correlations between E_{obs} and E_{calc} (*TRACOR*, Bruins Slot & Beurskens, 1987*b*). The fragment was expanded to the complete molecule with *DIRDIF* (Beurskens *et al.*, 1984).

Isotropic least-squares refinement (*SHELX*, Sheldrick, 1976) converged to $R = 0{\cdot}084$. H atoms were located from difference Fourier maps, and were assigned isotropic temperature factors of the parent atoms. At this stage an empirical absorption correction was applied (Walker & Stewart, 1983). Anisotropic refinement with fixed isotropic thermal parameters for the H atoms converged to $R = 0{\cdot}035$ and $wR = 0{\cdot}040$, $S = 1{\cdot}83$ for 2454 reflections and 343 variables using $w = 1/[\sigma^2(F) + 0{\cdot}0003F^2]$ with a maximum shift/e.s.d. = 0·37. Maximum electron density in the final difference Fourier map = 0·18 e Å^{-3}.

Pseudorotational phase angles and puckering amplitudes of the five-membered ring were calculated from the torsion angles (Altona & Sundaralingam, 1972; Rao, Westhof & Sundaralingam, 1981). Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974).

Discussion

The atomic coordinates and equivalent isotropic temperature factors are listed in Table 1* and a view of the molecule with the atomic numbering is presented in Fig. 1. From the figure it can be seen that the configuration at C(1) is β. This result confirms the tentative assignment of the configuration, which was based on Hudson's rules of isorotation (Ness, MacDonald & Fletcher, 1961). Bond lengths, bond angles and torsion angles are given in Table 2. A projection along the *c* axis of the unit cell is shown in Fig. 2. The packing of the molecule is limited to van der Waals radii. The observed bond lengths of the *p*-nitrobenzoyl substituents are in agreement with reported bond distances of crystalline *p*-nitrobenzoic acid (Sakora & Pant, 1966).

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å$^2 \times 10^2$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$$

	x	*y*	*z*	U_{eq}
C(1')	0·35705 (15)	0·69255 (19)	0·4597 (13)	7·68 (16)
O(1)	0·41732 (8)	0·70272 (9)	0·5901 (5)	5·47 (7)
C(1)	0·46589 (14)	0·70268 (13)	0·3775 (8)	5·18 (10)
C(2)	0·52670 (14)	0·71871 (13)	0·5334 (9)	5·36 (11)
C(3)	0·55557 (13)	0·65784 (14)	0·6205 (8)	4·50 (9)
O(3)	0·62119 (8)	0·65862 (8)	0·5193 (5)	4·79 (6)
C(4)	0·51713 (12)	0·61017 (12)	0·4491 (7)	4·09 (9)
O(4)	0·47620 (9)	0·64368 (8)	0·2487 (5)	4·92 (6)
C(5)	0·47963 (14)	0·56682 (13)	0·6446 (7)	4·63 (10)
O(5)	0·45434 (8)	0·51972 (8)	0·4468 (5)	4·85 (7)
C(11)	0·34285 (12)	0·36729 (11)	−0·1611 (6)	4·20 (9)
C(12)	0·40594 (12)	0·37841 (11)	−0·1109 (8)	4·52 (10)
C(13)	0·42260 (13)	0·42583 (12)	0·0817 (7)	4·52 (9)
C(14)	0·37544 (11)	0·46095 (11)	0·2167 (6)	3·85 (8)
C(15)	0·31260 (13)	0·44851 (13)	0·1602 (7)	4·40 (9)
C(16)	0·29530 (13)	0·40134 (13)	−0·0286 (8)	4·79 (10)
N(17)	0·32507 (12)	0·31583 (11)	−0·3630 (6)	5·45 (9)
O(18)	0·26957 (10)	0·30485 (13)	−0·3975 (8)	9·71 (12)
O(19)	0·36686 (11)	0·28763 (10)	−0·4878 (6)	7·84 (9)
C(20)	0·39195 (11)	0·51199 (12)	0·4301 (7)	4·10 (9)
O(21)	0·35313 (9)	0·54053 (9)	0·5678 (6)	5·96 (7)
C(31)	0·84353 (13)	0·62096 (14)	0·2566 (9)	5·77 (11)
C(32)	0·82609 (15)	0·57233 (16)	0·4385 (10)	6·74 (14)
C(33)	0·76604 (15)	0·57148 (13)	0·5535 (10)	6·28 (13)
C(34)	0·72328 (12)	0·61800 (12)	0·4918 (8)	4·65 (10)
C(35)	0·74265 (14)	0·66612 (14)	0·3092 (9)	5·57 (11)
C(36)	0·80257 (14)	0·66786 (14)	0·1926 (9)	6·09 (12)
N(37)	0·90770 (13)	0·62206 (15)	0·1282 (9)	8·06 (13)
O(38)	0·94314 (13)	0·58075 (16)	0·1954 (12)	14·20 (18)
O(39)	0·92184 (12)	0·66191 (14)	−0·0485 (10)	12·16 (16)
C(40)	0·65815 (13)	0·61388 (13)	0·6184 (8)	5·10 (10)
O(41)	0·64089 (10)	0·57417 (10)	0·7888 (6)	7·67 (9)
H(11')	0·3288 (14)	0·6960 (15)	0·634 (8)	7·21
H(12')	0·3547 (13)	0·6555 (15)	0·355 (8)	7·21
H(13')	0·3461 (14)	0·7282 (14)	0·350 (9)	7·21
H(1)	0·4557 (12)	0·7290 (12)	0·211 (8)	4·86
H(2)	0·5196 (12)	0·7425 (12)	0·699 (7)	4·92
H(2')	0·5580 (11)	0·7390 (12)	0·405 (7)	4·92
H(3)	0·5554 (11)	0·6517 (13)	0·825 (7)	4·34
H(4)	0·5448 (11)	0·5863 (11)	0·329 (7)	4·18
H(51)	0·5086 (11)	0·5463 (12)	0·785 (7)	4·51
H(52)	0·4452 (12)	0·5859 (11)	0·745 (7)	4·51
H(12)	0·4353 (11)	0·3581 (12)	−0·212 (7)	4·16
H(13)	0·4664 (12)	0·4363 (10)	0·123 (6)	4·24
H(15)	0·2812 (10)	0·4723 (11)	0·260 (7)	4·36
H(16)	0·2508 (12)	0·3928 (11)	−0·054 (6)	4·67
H(32)	0·8544 (13)	0·5447 (14)	0·488 (8)	6·67
H(33)	0·7521 (13)	0·5414 (13)	0·673 (8)	5·90
H(35)	0·7134 (11)	0·6941 (12)	0·263 (7)	5·25

The mean values of the C–C (1·509 Å) and non-acetal C–O (1·439 Å) distances in the sugar fragment agree well with the corresponding values in three different crystal structures of 1,2,3,5-tetra-*O*-acetyl-β-D-ribofuranose (James & Stevens, 1973; Poppleton, 1976; Czugler, Kálmán, Kováks & Pintér, 1981). However, accepting 1·43 Å as a standard value, the title compound displays a significantly shortened C(1)–O(1) bond (−0·04 Å) (Table 3). The conformation about this bond, as represented by the torsion angle O(4)–C(1)–O(1)–C(1'), is *gauche* (−68·2°). Examination of the torsion angle C(4)–O(4)–C(1)–O(1) (−84·2°) shows that the *endo* anomeric O(4)–C(1) bond can be described as a near-*gauche* conformation. A similar near-*gauche*/*gauche* conformation of the acetal centre was reported for the solid-state structures of the acetylated β-D-ribofuranoses (James & Stevens, 1973; Poppleton, 1976; Czugler, Kálmán, Kováks & Pintér, 1981). However, in contrast to our

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43408 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected interatomic distances* (Å), *bond angles* (°) *and torsion angles* (°), *with e.s.d.'s in parentheses*

C(1')–O(1)	1·413 (4)	C(14)–C(15)	1·376 (3)
O(1)–C(1)	1·389 (3)	C(14)–C(20)	1·500 (4)
C(1)–C(2)	1·497 (4)	C(15)–C(16)	1·375 (4)
C(1)–O(4)	1·426 (3)	N(17)–O(18)	1·205 (3)
C(2)–C(3)	1·513 (4)	N(17)–O(19)	1·209 (3)
C(3)–O(3)	1·455 (3)	C(20)–O(21)	1·195 (3)
C(3)–C(4)	1·522 (4)	C(31)–C(32)	1·381 (5)
O(3)–C(40)	1·325 (3)	C(31)–C(36)	1·370 (4)
C(4)–O(4)	1·437 (3)	C(31)–N(37)	1·468 (4)
C(4)–C(5)	1·506 (4)	C(32)–C(33)	1·365 (5)
C(5)–O(5)	1·451 (3)	C(33)–C(34)	1·386 (4)
O(5)–C(20)	1·329 (3)	C(34)–C(35)	1·386 (4)
C(11)–C(12)	1·372 (3)	C(34)–C(40)	1·486 (4)
C(11)–C(16)	1·379 (4)	C(35)–C(36)	1·366 (4)
C(11)–N(17)	1·483 (3)	N(37)–O(38)	1·209 (4)
C(12)–C(13)	1·385 (4)	N(37)–O(39)	1·206 (4)
C(13)–C(14)	1·391 (4)	C(40)–O(41)	1·205 (3)
C(1')–O(1)–C(1)	112·9 (3)	C(11)–C(16)–C(15)	117·9 (2)
O(1)–C(1)–C(2)	108·8 (3)	C(11)–N(17)–O(18)	118·2 (3)
O(1)–C(1)–O(4)	112·5 (2)	C(11)–N(17)–O(19)	118·4 (2)
C(2)–C(1)–O(4)	105·3 (2)	O(18)–N(17)–O(19)	123·4 (3)
C(1)–C(2)–C(3)	104·8 (2)	O(5)–C(20)–C(14)	111·1 (2)
C(2)–C(3)–O(3)	107·1 (2)	O(5)–C(20)–O(21)	125·7 (3)
C(2)–C(3)–C(4)	105·2 (3)	C(14)–C(20)–O(21)	123·2 (2)
O(3)–C(3)–C(4)	111·3 (3)	C(32)–C(31)–C(36)	121·8 (3)
C(3)–O(3)–C(40)	116·8 (2)	C(32)–C(31)–N(37)	118·8 (3)
C(3)–C(4)–O(4)	106·1 (2)	C(36)–C(31)–N(37)	119·3 (3)
C(3)–C(4)–C(5)	115·2 (3)	C(31)–C(32)–C(33)	118·3 (3)
O(4)–C(4)–C(5)	110·9 (2)	C(32)–C(33)–C(34)	121·4 (3)
C(1)–O(4)–C(4)	107·9 (2)	C(33)–C(34)–C(35)	118·6 (3)
C(4)–C(5)–O(5)	107·2 (2)	C(33)–C(34)–C(40)	118·9 (3)
C(5)–O(5)–C(20)	119·2 (2)	C(35)–C(34)–C(40)	122·5 (3)
C(12)–C(11)–C(16)	122·8 (3)	C(34)–C(35)–C(36)	120·9 (3)
C(12)–C(11)–N(17)	118·5 (2)	C(31)–C(36)–C(35)	119·0 (3)
C(16)–C(11)–N(17)	118·7 (2)	C(31)–N(37)–O(38)	117·6 (4)
C(11)–C(12)–C(13)	118·5 (3)	C(31)–N(37)–O(39)	119·3 (3)
C(12)–C(13)–C(14)	119·6 (2)	O(38)–N(37)–O(39)	123·0 (4)
C(13)–C(14)–C(15)	120·2 (3)	O(3)–C(40)–C(34)	112.1 (3)
C(13)–C(14)–C(20)	120·8 (2)	O(3)–C(40)–O(41)	124·0 (3)
C(15)–C(14)–C(20)	119·0 (2)	C(34)–C(40)–O(41)	123·9 (3)
C(14)–C(15)–C(16)	120·9 (3)		
C(1')–O(1)–C(1)–C(2)	175·5 (3)	C(1')–O(1)–C(1)–O(4)	−68·2 (3)
C(4)–O(4)–C(1)–C(2)	34·1 (3)	C(4)–O(4)–C(1)–O(1)	−84·2 (3)
O(1)–C(1)–C(2)–C(3)	92·7 (3)	O(4)–C(1)–C(2)–C(3)	−28·2 (3)
C(1)–C(2)–C(3)–C(4)	12·2 (3)	C(1)–C(2)–C(3)–O(3)	130·7 (3)
C(2)–C(3)–C(4)–C(5)	−115·5 (3)	C(2)–C(3)–C(4)–O(4)	7·6 (3)
O(3)–C(3)–C(4)–C(5)	128·8 (3)	O(3)–C(3)–C(4)–O(4)	−108·0 (2)
C(3)–C(4)–C(5)–O(5)	−171·5 (2)	O(4)–C(4)–C(5)–O(5)	68·1 (3)
C(3)–C(4)–O(4)–C(1)	−26·0 (3)	C(5)–C(4)–O(4)–C(1)	99·8 (3)
C(5)–O(5)–C(20)–C(14)	−179·5 (2)	C(5)–O(5)–C(20)–O(21)	−0·6 (4)
C(2)–C(3)–O(3)–C(40)	168·8 (3)	C(4)–C(3)–O(3)–C(40)	−76·7 (3)
C(3)–O(3)–C(40)–C(34)	177·9 (2)	C(3)–O(3)–C(40)–O(41)	−1·5 (4)
O(21)–C(20)–C(14)–C(15)	4·3 (4)	O(5)–C(20)–C(14)–C(13)	4·3 (4)
O(3)–C(40)–C(34)–C(35)	4·2 (4)	O(41)–C(40)–C(34)–C(33)	4·8 (5)
C(12)–C(11)–N(17)–O(19)	−3·7 (4)	C(16)–C(11)–N(17)–O(18)	−1·8 (4)
C(23)–C(31)–N(37)–O(38)	−2·0 (6)	C(36)–C(31)–N(37)–O(39)	−5·2 (6)

finding of a shortened *exo* anomeric bond in methyl 2-deoxy-β-D-ribofuranoside, in the acetylated β-D-ribofuranoses a significantly shortened (−0·03 Å) *endo* anomeric bond O(4)–C(1) is apparent (Table 3).

At this point comparison with other anomeric fragments is appropriate. By far the largest body of information concerning acetal C–O bond lengths is found in X-ray structures of glycopyranosides. Inspection of Table 3 shows that the *exo* anomeric bond is shortened in the structures of methyl α-D-glycopyranosides, whereas the *endo* anomeric bond is shortened in the structures of acetylated α-D-glycopyranoses. As can be gleaned from Table 3, the mean value for both the endocyclic and the exocyclic C–O bond lengths in three different crystal structures of acetyl β-D-ribofuranosides accords well with mean distances observed for the corresponding bonds in nine different crystal structures of acetyl α-D-glycopyranosides. However, a similar agreement in bond lengths is not found when the data for the acetyl β-D-ribofuranosides, which display near-*gauche*/*gauche* conformations around O(4)–C(1)–O(1), are compared with those for acetyl β-D-glycopyranosides that have near-*trans*/*gauche* conformations around O(5)–C(1)–O(1). Taken together, the data show that there is a correlation between the conformation of the acetal centre and the observed bond shortening.

An explanation for the dependency of bond shortening on both the conformation of the anomeric moiety and the nature of the glycosyl substituent has been suggested by Altona (1964); see also Romers, Altona, Buijs & Havinga (1969). In this concept the nonbonding electrons on the O atom are delocalized by mixing with a suitably (*i.e. anti*) oriented and

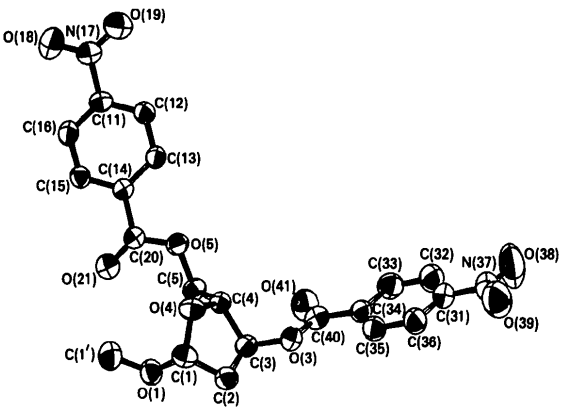

Fig. 1. *ORTEP* (Johnson, 1965) diagram and atomic numbering for methyl 2-deoxy-3,5-di-*O*-*p*-nitrobenzoyl-β-D-ribofuranoside. H atoms have been omitted.

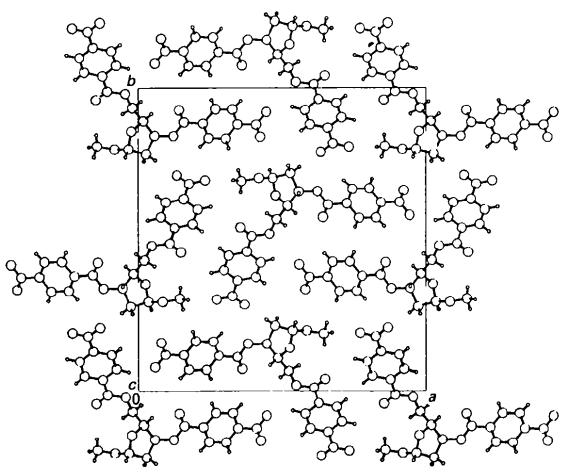

Fig. 2. *PLUTO* (Motherwell, 1976) diagram of the packing of the molecules in the unit cell projected on the *ab* plane.

Table 3. *Comparison of conformation and bond distances about the anomeric centre of the title compound with those of similar molecules*

Numbers in parentheses are e.s.d. values, numbers in square brackets are r.m.s. standard deviations. Mean values for n structures are given for (*a*) acetyl β-D-ribofuranosides (James & Stevens, 1973; Poppleton, 1976; Czugler, Kálmán, Kováks & Pintér, 1981), (*b*) methyl α-D-glycopyranosides (Jeffrey, Pople, Binkley & Vishveshwara, 1978), (*c*) acetyl α-D-pyranosides (Jeffrey & Yates, 1980), (*d*) methyl β-D-glycopyranosides (Jeffrey, Pople, Binkley & Vishveshwara, 1978), and (*e*) acetyl β-D-glycopyranosides (Jeffrey & Yates, 1980).

		Conformation of the acetal-centre torsion angles (°)		Bond distances of the anomeric moiety (Å)			
	n	C(4)–O(4)–C(1)–O(1)	O(4)–C(1)–O(1)–R	C(4)–O(4)	O(4)–C(1)	C(1)–O(1)	O(1)–R
Title compound	1	−84·2 (3)	−68·2 (3)	1·437 (3)	1·426 (3)	1·389 (3)	1·413 (4)
(*a*)	3	−97 [3]	−80 [3]	1·450 [13]	1·398 [5]	1·440 [7]	1·359 [12]
		C(5)–O(5)–C(1)–O(1)	O(5)–C(1)–O(1)–R	C(5)–O(5)	O(5)–C(1)	C(1)–O(1)	O(1)–R
(*b*)	8	+61 [2]	+65 [3]	1·435 [9]	1·416 [3]	1·403 [7]	1·431 [6]
(*c*)	9	+65 [3]	+86 [3]	1·438 [4]	1·397 [7]	1·436 [9]	1·357 [15]
(*d*)	9	+177 [3]	−78 [5]	1·433 [6]	1·428 [6]	1·383 [7]	1·427 [4]
(*e*)	3	+179 [1]	−90 [7]	1·425 [4]	1·414 [6]	1·411 [5]	1·355 [10]

'low-lying' antibonding σ^* orbital of the ligand bond. Bond shortening is predicted to occur between the lone-pair-donating atoms [O(1) and/or O(4)] and the acceptor atom [C(1)]. In terms of this theory, the atom which behaves as the dominant lone-pair donor is O(1) for the title compound, whereas in the acetylated β-D-ribofuranosides O(4) acts as the lone-pair donor. This difference may reflect the influence of the substituent at O(1) (methyl *vs* acetyl).

Conformation of the sugar ring

It has been shown that a five-membered ring can be described in terms of two degrees of freedom for ring puckering, usually represented by a puckering amplitude (φ_m) and a phase angle (P) (Altona, Geise & Romers, 1968; Altona & Sundaralingam, 1972). The endocyclic torsion angles (φ_j) of a five-membered ring are mutually related by the well-known pseudorotation equation of Altona & Sundaralingam (1972):

$$\varphi_j = \varphi_m \cos(P + 4\pi j/5) \quad j = 0 \ldots 4 \qquad (1)$$

In this equation φ_0 is chosen as the endocyclic torsion about the bond C(2)–C(3). The remaining endocyclic torsion angles φ_1–φ_4 are assigned clockwise to C(3)–C(4), C(4)–O(4), O(4)–C(1) and C(1)–C(2).

The results of a pseudorotational analysis (Altona & Sundaralingam, 1972; Rao, Westhof & Sundaralingam, 1981) for the present molecule show that the conformation of the sugar ring can be characterized by a phase angle $P = -68{\cdot}3°$ and puckering amplitude $\varphi_m = 33{\cdot}7°$. This ring conformation can also be described as an intermediate conformation between the ${}^1_0T$ and ${}^1E$ puckerings (${}^1T_0$).

In view of our study of base-deleted oligonucleotides, it is of interest to compare the general behaviour of ring puckering in glycofuranosides with that of nucleoside derivatives. Pseudorotational analysis of the furanose ring for 1,2,3,5-tetra-*O*-acetyl-β-D-ribofuranose (*A* form: Czugler, Kálmán, Kováks & Pintér, 1981; *B* form: James & Stevens, 1973; Poppleton, 1976) and that for methyl 1,2,3,5-tetra-*O*-acetyl-β-D-galactofuranuronate (Beale, Stephenson & Stevens, 1971) shows that the five-membered rings in these molecules are characterized by P values of −10·7, −3·9, −4·9 and −58·7°, and φ_m values of 34·6, 38·0, 38·4 and 34·4°, respectively. A statistical study of 178 crystal structures of ribo-, 2′-deoxyribo- and arabinonucleoside derivatives (de Leeuw, Haasnoot & Altona, 1980) reveals that only two of them possess a negative pseudorotation phase angle: −10 and −24°. Hence, the calculated P values for glycofuranosides clearly fall outside the usual range observed for nucleoside derivatives, which probably reflects the larger influence of the anomeric effect manifest in glycofuranosides (in comparison with N-nucleosides) on the conformation of the five-membered ring. Another approach to show possible conformational differences between glycofuranosides and nucleoside derivatives is to compare observed and recalculated geometrical parameters from P and φ_m, using empirical pseudorotational equations. Firstly, a torsion angle equation was applied, which is in fact an improved form of (1) (de Leeuw, van Kampen, Altona, Diéz & Esteban, 1984). In the latter study additional correction terms were used, which were obtained from a regression analysis of the 178 X-ray crystal structures mentioned before. It is concluded from the excellent agreement between the observed and calculated torsion angles ($\Delta\varphi_j \leq 0{\cdot}1°$) that the empirical formalism of de Leeuw *et al.* describes the conformation of the 2-deoxy-β-D-ribofuranoside ring very well. From the same data set a function relating the endocyclic bond angles to P and φ_m has been parametrized (de Leeuw, van Kampen, Diéz & Esteban, 1984). Subtraction of calculated bond angles θ_j from the corresponding experimental values yields small, but significant, differences for the angles C(1)–C(2)–C(3) ($\Delta\theta = 1{\cdot}6°$) and C(2)–C(3)–C(4) ($\Delta\theta = 0{\cdot}8°$).

Recently, an empirical equation was derived, which relates the different endocyclic bond lengths L_j of the furanose ring to P (at $\varphi_m = 38{\cdot}7°$) (Pearlman & Kim, 1985). The coefficients of this function were determined from the empirical behaviour of the endocyclic

valence bond angles in X-ray structures of ribonucleos(t)ide derivatives (Westhof & Sundaralingam, 1980) and from geometrical constraints due to ring closure. Hence, for the title compound discrepancies between experimental and calculated bond lengths might be expected in view of the observed differences between the bond angles centred on C(2) and C(3). Indeed, a comparison between experimental and calculated bond lengths shows differences for C(1)–O(4) ($L_{obs} - L_{calc} = 0{\cdot}04$ Å) and C(2)–C(3) ($L_{obs} - L_{calc} = -0{\cdot}04$ Å). Remarkably, the mean endocyclic bond lengths of the acetylated β-D-riboses accord well with the corresponding calculated values. These observations demonstrate again the important influence of the substituent at C(1) on the conformation of the five-membered ring.

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Book Reviews

Works intended for notice in this column should be sent direct to the Book-Review Editor (J. H. Robertson, School of Chemistry, University of Leeds, Leeds LS2 9JT, England). As far as practicable books will be reviewed in a country different from that of publication.

Acta Cryst. (1987). B**43**, 223-224

Design, construction and properties of novel protein molecules. Proceedings of a Royal Society Discussion Meeting organized and edited by D. M. BLOW, A. R. FERSHT and G. WINTER. Pp. 159. London: The Royal Society, 1986. Price £27.50.

One of the most intriguing branches of modern molecular science is the 'engineering' of proteins. This is the controlled manipulation of the structure of protein molecules so as to produce, by design, new protein materials - especially new enzymes - for specific medical, pharmacological, industrial or other commercial application.

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