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Carbohydrate Orthoesters. III.* The Crystal and Molecular Structure of 3,4,6-Tri-*O*-acetyl-1,2-*O*-[1-(*exo*-ethoxy)ethylidene]-α-D-glucopyranose†

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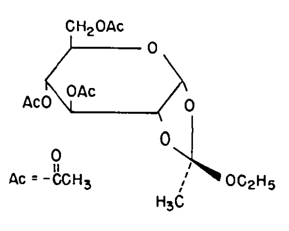
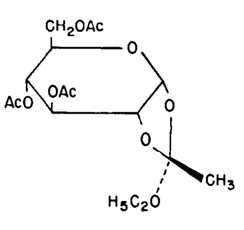
3,4,6-Tri-*O*-acetyl-1,2-*O*-[1-(*exo*-ethoxy)ethylidene]-α-D-glucopyranose ($C_{16}H_{24}O_{10}$) crystallizes in the monoclinic space group, $P2_1$, with $Z=2$ and cell parameters $a=7{\cdot}649$ (4), $b=14{\cdot}465$ (5), $c=8{\cdot}213$ (3) Å, and $\beta=96{\cdot}26$ (7)° at the experimental temperature of about −193 °C. The structure was solved using Patterson search and tangent formula methods. Block-diagonal least-squares refinement, with fixed hydrogen parameters, resulted in a final R index of 0·068 for 1680 observed reflections. The diastereoisomer investigated, which exhibits a p.m.r. methyl singlet at δ 1·71 p.p.m. ($CDCl_3$), has the (S)-configuration at the dioxolane-2-carbon atom, *i.e.*, the ethoxy substituent is *trans* or *exo* to the pyranoid ring. The dioxolane ring has an envelope conformation, with O(2) deviating 0·46 Å from the plane of the other four atoms toward the glucose-ring side of the plane. There are considerable structural differences in the O(1) and O(2) sides of the dioxolane ring. The pyranoid ring approximates a skew ($^3S_5$) conformation with some additional flattening in the vicinity of C(1) and C(2) due to the presence of the dioxolane ring. The solution p.m.r. data are consistent with the pyranoid-ring conformation found in the crystal structure.

Introduction

During the formation of 3,4,6-tri-*O*-acetyl-1,2-(1-ethoxyethylidene)-α-D-glucopyranose and similar orthoacylates, an asymmetric center evolves at the dioxolane-2-carbon atom, resulting in the possibility of two diastereoisomers, the *exo*- (I) and *endo*-alkoxy (II) isomers. In proton magnetic resonance (p.m.r.) spectra, the singlets attributable to the methyl groups attached to the dioxolane-2-carbon atoms of the isomeric orthoacetates appear at high field and are well resolved (Lemieux & Morgan, 1965). This crystal structure investigation was to determine the configuration at the dioxolane-2-carbon atom of one of the two diastereomers, and also aid in interpreting the p.m.r. data related to the conformation of the pyranoid ring. Coxon & Hall (1964) predicted skew conformations for related 1,2-*O*-alkylidene-α-D-glucopyranose derivatives which have similar ring structures and p.m.r. coupling constants. Lemieux & Morgan (1965) subsequently predicted flattened-chair conformations for the pyranoid rings of several acetylated 1,2-*O*-(1-alkoxyethylidene)-α-D-glucopyranoses, including (I). Trotter & Fawcett (1966) showed such a flattened-chair conformation in the crystal structure of the hydroiodide derivative of 1,2-*O*-(2-amino-1-methylethylidene)-α-D-glucopyranose and indicated that the p.m.r. data of Coxon & Hall (1964) for the parent amine could be reinterpreted reasonably well in terms of a flattened-chair conformation. Thus, since the p.m.r. data for many of the 1,2-*O*-alkylidene and 1,2-*O*-(1-alkoxy-alkylidene) derivatives of α-D-glucopyranose are similar, later workers (Rees, Tatchell & Wells,



(I)



(II)

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* Part II: Hultman, Schroeder & Haigh (1972).

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1967; Lemieux & Detert, 1968) have concluded that the conformations of the pyranoid rings in these compounds are similar and are of the flattened-chair type.

The orthoester (I), m.p. 96–98 °C, was synthesized as described by Schroeder, Hultman & Johnson (1972). Crystals (colorless prisms) for X-ray analysis were obtained by evaporation of a saturated solution of the orthoester in isopropyl ether–absolute ethanol (3:1, vol.), with a trace of pyridine to prevent acid-catalyzed reactions. Crystal density was measured by pycnometry using n-hexane. The crystals were selected and mounted in glass capillaries under low humidity conditions. Unit-cell parameters were determined at both room and low temperature.

Crystal data

$C_{16}H_{24}O_{10}$, F.W. 376·36, $F(000)=400$. Monoclinic space group $P2_1$; systematic extinctions $0k0$ with k odd. At 20°C: $a=7·791$ (2), $b=14·740$ (5), $c=8·281$ (4) Å, $\beta=96·91$ (5)°, $V=944·1$ (6) Å^3, $D_m=1·33$ g cm^{-3}, $D_x=1·357$ g cm^{-3}, $Z=2$, $\mu(\text{Cu } K\alpha)=10·0$ cm^{-1}. At -193°C: $a=7·649$ (4), $b=14·465$ (5), $c=8·212$ (3) Å, $\beta=96·26$ (7)°, $V=903·1$ Å^3, $D_x=1·418$ g cm^{-3}, $Z=2$, $\mu(\text{Cu } K\alpha)=10·4$ cm^{-1}.

Intensity data were collected near -193° with Ni-filtered Cu $K\alpha$ radiation and a liquid nitrogen gas flow cryostat (Richards, 1964). Multiple-film equi-inclination Weissenberg photographs were taken along the a axis through the fourth layer, and along the c axis through the fifth layer. Five crystals were used because traces of moisture in capillaries caused slow crystal decomposition.

Intensities were estimated visually by comparison with a calibrated film strip, and the data were corrected for spot size and Lorentz–polarization effects. Interlayer scaling was by the method of Rae (1965, 1966) and Moran (1972), and absolute scaling was by the K-curve method (Karle & Karle, 1966). Data reduction gave 1942 independent structure magnitudes of which 240 were unobserved. Average values for $|E^2|$, $|E^2-1|$, and $|E|$ were 0·998, 0·751, and 0·884 as compared with 1·000, 0·763, and 0·886 expected for non-centrosymmetric space groups.

P.m.r. spectra were determined in $CDCl_3$ on a Varian A-60A spectrometer at *ca* 40°C with tetramethylsilane as the internal standard.

Structure determination and refinement

Attempts to solve the structure by symbolic addition (Karle & Karle, 1966) and tangent formula (Karle, 1968) methods failed to provide a structure solution, although reasonable molecular fragments were located. The structure was solved by a combination of Patterson searching and tangent formula techniques. A four-atom model for an acetoxy group ($OCOCH_3$) was positioned using a Patterson search technique (Braun, Hornstra & Leenhouts, 1969). Phases were calculated from the four-atom fragment and were used to initiate successive tangent formula cycles (Karle, 1968) which gave a large, falsely located fragment containing only one of the four atoms used to initiate the phase determination. Thirteen atoms from the fragment were used as an input model for the Patterson searching program. The search confirmed a correct orientation, but clearly indicated a new location with respect to the screw axis. An additional tangent formula cycle gave the correct structure. In retrospect, it seems possible that some of the larger fragments from symbolic addition attempts could have been repositioned using Patterson searching techniques.

Refinement was by the block-diagonal least-squares program by Ahmed, Hall, Pippy & Huber (1966), and based on Cruickshank's (1970) treatment. Scattering factors used were those calculated by Stewart, Davidson & Simpson (1965) for the bonded hydrogen atom, and those calculated by Hanson, Herman, Lea & Skillman (1964) for carbon and oxygen.

Fifteen observed and three unobserved reflections of the $\bar{8}k1$ and $\bar{9}k1$ type were eliminated from the refinement because of errors in the intensity estimates, which had become apparent during data reduction. After isotropic and anisotropic refinement, hydrogen atoms were located in two successive difference syntheses. Although some of the methyl hydrogens were difficult to locate, the methine hydrogens were well resolved. Hydrogen atoms were assigned the isotropic temperature factors of the carbon atoms to which they were bonded, and all hydrogen parameters were held constant throughout the remainder of refinement. Additional anisotropic refinement was performed, after which five observed reflections were eliminated because of extinction effects, leaving a set of 1682 observed reflections for refinement.

The refinement minimized the quantity $R'=\sum W(|F_o|-|F_c|)^2$. After the grouping of the data according to F_o and analysis of the average R' as a function of the average $|F_o|$ of each group, weights, W_F, were determined so that R' was constant when analyzed as a function of average $|F_o|$, and these weights were then applied to the data.

$$W_F=[2·21-0·165|F_o|+0·00737|F_o|^2]^{-1}. \quad (1)$$

After application of the weights W_F to the data, the data were analyzed as a function of $\sin\theta$, and the weighting scheme W_θ was determined.

$$W_\theta=[3·79-10·2\sin\theta+8·19\sin^2\theta]^{-1}. \quad (2)$$

The final weighting scheme applied was the product $W=(W_F)(W_\theta)$. Ten cycles of anisotropic refinement reduced R to its final value of 0·068 for 1680 observed reflections.*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30519 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Results

The atomic numbering scheme assigned to the molecule is shown in Fig. 1. The fractional atomic coordinates, anisotropic temperature factors, and isotropic temperature factors are given in Table 1 for non-hydrogen atoms. All fractional coordinates are for a single molecule of the D-glucose enantiomorph, since the molecule is known to have that absolute configuration. Bond distances and angles for the non-hydrogen atoms are given in Table 2. Average estimated standard deviations for C–C and C–O bond distances, and for angles between such bonds were 0·008 Å, 0·007 Å, and 0·4°, respectively. Unrefined fractional coordinates for hydrogen atoms, and C–H bond lengths are given in Table 3.

Thermal motion ellipsoids were calculated for each non-hydrogen atom by the method proposed by Waser (1955), and modified by Busing & Levy (1958). Thermal ellipsoid volumes ranged from 232×10^{-5} to 1440×10^{-5} Å^3, with an average value of 756×10^{-5} Å^3, which is a distribution similar to those found in other similar low-temperature investigations (Ham & Williams, 1970; Scott & Richards, 1971). Low volumes were associated with atoms incorporated into the ring structure, or attached to three or more carbon or oxygen atoms by covalent bonds, while higher volumes were associated with those atoms further from the ring structure. Such behavior reflects the expected rigidity of the covalent bond scheme, but is also consistent with oscillation of the molecule as a rigid body.

Discussion

Description of the pyranoid moiety

When compared to a survey of 27 pyranoid rings by Arnott & Scott (1972), the bond distances of the glucose ring are similar to those found in 15 α-glycosides. The exocyclic C(5)–C(6) bond is 0·03 Å shorter than the average C–C bond length in the pyranoid ring (1·530 Å), which is in agreement with the findings of the survey (Arnott & Scott, 1972) and of Ham & Williams (1970). Angles in the pyranoid ring at C(1),

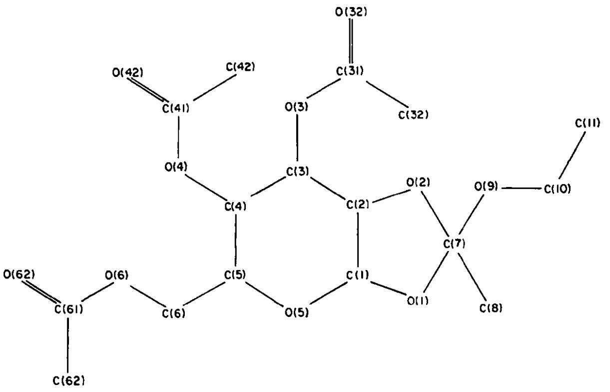

Fig. 1. Atomic numbering scheme. Hydrogen atoms, eliminated for simplicity, are assigned the same numbers as the carbon atoms to which they are attached. When more than one hydrogen atom has the same number, they are arbitrarily identified by the addition of the letters *A*, *B*, and *C*.

Table 1. *Atomic coordinates and temperature factors for the carbon and oxygen atoms*

Estimated standard deviations given in parentheses refer to the least significant figures in the parameter values. Temperature factors are given for the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{23}kl+\beta_{13}hl+\beta_{12}hk)\times10^{-4}]$. B_i are the isotropic temperature factors determined during isotropic refinement.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}	B_i
C(1)	0·2521 (7)	−0·0503 (4)	0·4481 (6)	52 (9)	13 (2)	22 (7)	7 (7)	12 (13)	−5 (8)	0·540
C(2)	0·2081 (7)	0·0531 (4)	0·4555 (6)	35 (8)	16 (2)	12 (6)	−10 (7)	27 (12)	4 (8)	0·458
C(3)	0·3049 (7)	0·1132 (4)	0·3428 (6)	72 (10)	11 (2)	31 (7)	8 (7)	17 (14)	−5 (8)	0·725
C(4)	0·3159 (7)	0·0721 (4)	0·1727 (6)	59 (9)	14 (3)	29 (7)	−3 (7)	9 (13)	−13 (8)	0·697
C(5)	0·2636 (7)	−0·0304 (4)	0·1629 (6)	61 (9)	14 (3)	23 (7)	−5 (7)	34 (13)	5 (8)	0·748
C(6)	0·3365 (8)	−0·0781 (4)	0·0228 (6)	97 (10)	12 (2)	39 (5)	−4 (7)	33 (15)	−26 (9)	1·039
C(7)	−0·0474 (7)	−0·0254 (4)	0·4508 (6)	42 (9)	11 (2)	39 (7)	−4 (7)	42 (13)	3 (7)	0·752
C(8)	−0·2102 (8)	−0·0479 (4)	0·3423 (7)	85 (10)	14 (2)	37 (7)	11 (7)	25 (15)	−12 (9)	1·042
C(10)	−0·1356 (9)	−0·0912 (5)	0·6992 (7)	157 (13)	18 (3)	52 (8)	17 (8)	72 (18)	−7 (11)	1·696
C(11)	−0·1856 (8)	−0·0599 (5)	0·8601 (7)	77 (10)	38 (4)	49 (8)	19 (9)	20 (16)	−36 (10)	1·856
C(31)	0·5109 (7)	0·1984 (4)	0·5192 (6)	48 (8)	14 (2)	22 (7)	4 (7)	50 (13)	18 (8)	0·648
C(32)	0·6967 (8)	0·2010 (4)	0·5936 (7)	75 (10)	18 (3)	46 (8)	−13 (8)	−34 (15)	−10 (9)	1·195
C(41)	0·2555 (8)	0·1497 (4)	−0·0858 (7)	81 (10)	14 (3)	35 (7)	17 (7)	−15 (14)	−40 (8)	0·806
C(42)	0·1199 (8)	0·2022 (4)	−0·1892 (7)	89 (10)	16 (3)	36 (7)	3 (7)	17 (15)	15 (9)	1·143
C(61)	0·3152 (8)	−0·2237 (4)	−0·1075 (6)	88 (10)	20 (3)	23 (7)	−14 (7)	25 (14)	−4 (9)	1·060
C(62)	0·2257 (8)	−0·3149 (4)	−0·1161 (7)	100 (11)	17 (3)	63 (9)	−33 (8)	67 (16)	−5 (9)	1·462
O(1)	0·0836 (5)	−0·0938 (3)	0·4383 (4)	60 (6)	10 (2)	39 (5)	5 (5)	29 (9)	3 (6)	0·700
O(2)	0·0269 (5)	0·0580 (3)	0·4018 (4)	51 (6)	8 (2)	35 (5)	4 (5)	44 (9)	1 (5)	0·548
O(3)	0·4827 (5)	0·1238 (3)	0·4202 (4)	46 (6)	11 (2)	38 (5)	−11 (5)	20 (9)	2 (5)	0·714
O(4)	0·1995 (5)	0·1241 (3)	0·0584 (4)	75 (7)	16 (2)	25 (5)	3 (5)	20 (10)	4 (6)	0·881
O(5)	0·3354 (5)	−0·0737 (3)	0·3103 (4)	62 (6)	14 (2)	26 (5)	0 (5)	17 (9)	0 (6)	0·790
O(6)	0·2560 (5)	−0·1682 (3)	0·0051 (4)	81 (7)	13 (2)	34 (5)	−16 (5)	46 (10)	−17 (6)	0·889
O(9)	−0·0751 (5)	−0·0121 (3)	0·6154 (4)	70 (7)	14 (2)	21 (5)	1 (5)	55 (9)	−11 (6)	0·780
O(32)	0·3990 (5)	0·2550 (3)	0·5371 (4)	62 (7)	15 (2)	38 (5)	−9 (5)	36 (10)	14 (6)	1·038
O(42)	0·4011 (5)	0·1289 (3)	−0·1233 (5)	73 (7)	28 (2)	48 (5)	19 (6)	48 (10)	1 (7)	1·389
O(62)	0·4269 (7)	−0·1997 (3)	−0·1916 (6)	150 (9)	30 (2)	91 (7)	−63 (7)	179 (14)	−49 (8)	2·029

C(2), and C(3) appear significantly larger ($3{\cdot}3\sigma$, $2{\cdot}8\sigma$, and $2{\cdot}8\sigma$, respectively) than the average values of 109·2°, 110·5°, and 110·5° found by Arnott & Scott (1972). The angle at O(5) appears normal for an α-sugar, but the angle at C(4) is somewhat larger than the expected 110·3°, and the angle at C(5) is somewhat smaller than the expected 110·0° angle. Bond distances and angles in the three substituents attached at C(3), C(4), and C(5) all appear normal, except for the angle of 107·7° at C(6), which is $3{\cdot}4\sigma$ smaller than the average angle of 111·8° found in 23 other pyranose derivatives (Arnott & Scott, 1972).

Table 2. *Interatomic distances* (Å) *and angles* (°)

Standard deviations for the last decimal place of each distance and angle are shown in parentheses.

C(1)—C(2)	1·536 (8)	O(1)—C(1)—C(2)	103·4 (4)
C(2)—C(3)	1·521 (7)	C(1)—C(2)—O(2)	104·4 (4)
C(3)—C(4)	1·529 (7)	C(2)—O(2)—C(7)	106·3 (4)
C(4)—C(5)	1·535 (8)	O(2)—C(7)—O(1)	105·4 (4)
C(5)—C(6)	1·500 (8)	C(7)—O(1)—C(1)	109·2 (4)
C(7)—C(8)	1·486 (8)	O(5)—C(1)—O(1)	109·6 (4)
C(10)–C(11)	1·486 (9)	C(3)—C(2)—O(2)	107·9 (4)
C(31)–C(32)	1·485 (8)	O(1)—C(7)—C(8)	110·9 (4)
C(41)–C(42)	1·478 (8)	O(1)—C(7)—O(9)	110·3 (4)
C(61)–C(62)	1·485 (9)	O(2)—C(7)—C(8)	110·7 (4)
C(1)—O(5)	1·399 (6)	O(2)—C(7)—O(9)	105·3 (4)
C(5)—O(5)	1·420 (6)	C(8)—C(7)—O(9)	113·8 (4)
C(1)—O(1)	1·429 (6)	C(7)—O(9)—C(10)	116·2 (4)
C(2)—O(2)	1·410 (6)	O(9)—C(10)–C(11)	108·1 (5)
C(7)—O(1)	1·420 (6)	C(2)—C(3)—O(3)	106·8 (4)
C(7)—O(2)	1·411 (6)	C(4)—C(3)—O(3)	107·5 (4)
C(7)—O(9)	1·404 (6)	C(3)—C(4)—O(4)	107·6 (4)
C(10)–O(9)	1·437 (8)	C(5)—C(4)—O(4)	109·4 (4)
C(3)—O(3)	1·445 (7)	C(4)—C(5)—C(6)	111·6 (4)
C(4)—O(4)	1·434 (6)	O(5)—C(5)—C(6)	108·0 (4)
C(6)—O(6)	1·442 (7)	C(5)—C(6)—O(6)	107·7 (4)
C(31)–O(3)	1·354 (6)	C(3)—O(3)—C(31)	115·4 (4)
C(41)–O(4)	1·354 (6)	C(4)—O(4)—C(41)	118·9 (4)
C(61)–O(6)	1·340 (7)	C(6)—O(6)—C(61)	116·0 (4)
C(31)–O(32)	1·205 (7)	O(3)—C(31)–C(32)	110·5 (4)
C(41)–O(42)	1·225 (7)	O(4)—C(41)–C(42)	112·0 (5)
C(61)–O(62)	1·207 (8)	O(6)—C(61)–C(62)	112·1 (5)
		O(3)—C(31)–O(32)	123·1 (5)
O(5)–C(2)–C(1)	112·9 (4)	O(4)—C(41)–O(42)	122·4 (5)
C(1)–C(2)–C(3)	114·2 (4)	O(6)—C(61)–O(62)	122·5 (5)
C(2)–C(3)–C(4)	114·4 (4)	C(32)–C(31)–O(32)	126·4 (5)
C(3)–C(4)–C(5)	112·6 (4)	C(42)–C(41)–O(42)	125·6 (5)
C(4)–C(5)–O(5)	107·9 (4)	C(62)–C(61)–O(62)	125·4 (6)
C(5)–O(5)–C(1)	114·5 (4)		

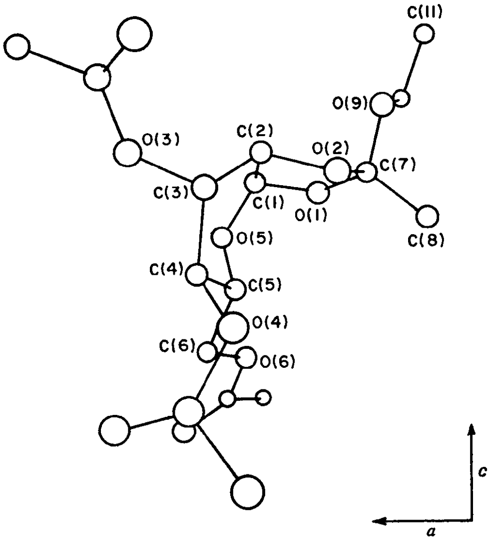

Fig. 2. Perspective view from +**b** direction, showing the ring conformations and the isomeric configuration.

Table 3. *Unrefined hydrogen coordinates and carbon–hydrogen bond lengths* (Å)

	x	y	z	B_{iso}	C–H
H(1)	0·319	−0·070	0·562	0·54	1·1
H(2)	0·217	0·098	0·550	0·46	1·0
H(3)	0·264	0·172	0·316	0·73	0·9
H(4)	0·444	0·085	0·162	0·70	1·0
H(5)	0·127	−0·038	0·150	0·75	1·0
H(6*A*)	0·294	−0·041	−0·076	1·04	1·0
H(6*B*)	0·458	−0·086	0·036	1·04	0·9
H(8*A*)	−0·250	−0·110	0·354	1·04	1·0
H(8*B*)	−0·181	−0·046	0·220	1·04	1·1
H(8*C*)	−0·319	−0·009	0·374	1·04	1·1
H(10*A*)	−0·021	−0·144	0·726	1·70	1·2
H(10*B*)	−0·242	−0·134	0·636	1·70	1·1
H(11*A*)	−0·056	−0·025	0·942	1·86	1·2
H(11*B*)	−0·292	−0·029	0·844	1·86	0·9
H(11*C*)	−0·240	−0·109	0·944	1·86	1·1
H(32*A*)	0·698	0·242	0·688	1·20	1·0
H(32*B*)	0·756	0·134	0·616	1·20	1·1
H(32*C*)	0·738	0·231	0·470	1·20	1·2
H(42*A*)	0·077	0·242	−0·114	1·14	0·9
H(42*B*)	0·173	0·235	−0·286	1·14	1·1
H(42*C*)	0·035	0·165	−0·228	1·14	0·9
H(62*A*)	0·244	−0·352	−0·202	1·46	0·9
H(62*B*)	0·090	−0·309	−0·126	1·46	1·0
H(62*C*)	0·244	−0·346	−0·008	1·46	1·0

Comparison of the torsion angles of the pyranoid ring of the orthoester (I) with those for a normal chair ($^4C_1$) conformation (Table 4) indicates the C(2)–C(3) conformational inversion predicted by Coxon & Hall (1964) for similar molecules. The conformation is best described as a skew conformation ($^3S_5$) with some flattening in the vicinity of C(1) and C(2) (Table 4, Fig. 2). The flattening is not unexpected since restrictions are imposed on the pyranoid system by fusion of the dioxolane ring at C(1) and C(2). The torsion angles involving pyranoid ring hydrogen atoms of (I) (Table 4) also indicate the $^3S_5$ character of the ring conformation.

The pyranoid ring, as expected since it closely approximates an $^3S_5$ conformation, has two approximately planar arrangements of four ring atoms which are described by equations (3) and (4). The angle between the two planes C(1), C(2), C(4), O(5):

$$-0{\cdot}8612X'-0{\cdot}2332Y-0{\cdot}4517Z'=-2{\cdot}8474 \qquad (3)$$

and C(1), C(3), C(4), C(5):

$$-0{\cdot}9713X'+0{\cdot}1803Y-0{\cdot}1550Z'=-2{\cdot}1550 \qquad (4)$$

is 30°, and the root-mean-square deviations of the atoms in the two planes are 0·032 and 0·053 Å, respectively.

The skew conformation of the glucopyranose ring results in the C(3) acetoxy group having an axial orientation, while the C(4) acetoxy group has a quasi orientation. The C(5) acetoxymethyl substituent has an equatorial orientation.

Of considerable interest with respect to a later discussion of the p.m.r. analysis of the orthoester is the approximately planar ('W') arrangement of H(2)–C(2)–C(3)–C(4)–H(4), in which H(4) is slightly out of the plane of the other four atoms because of its quasi orientation. The conformation angles for this system are 179° for H(2)–C(2)–C(3)–C(4) and 166° for C(2)–C(3)–C(4)–H(4), indicating that the system is essentially planar.

Description of the dioxolane moiety

Structural differences exist in the O(1) and O(2) sides of the dioxolane ring. The two bonds at O(2) are almost identical in length, and appear somewhat shorter than the two bonds at O(1). The 109·2° angle at O(1) is significantly larger than the 106·3° angle at O(2). Although the angles O(1)–C(7)–C(8) and O(2)–C(7)–C(8) are approximately equal, there seems to be a highly significant difference (12·5σ) between the value of 110·3° for O(1)–C(7)–O(9) and the value of 105·3° for O(2)–C(7)–O(9). Although these structural differences are large, steric accessibility of O(1) and O(2), which could be important in acid-catalyzed reactions, seems about equal, when judged by visual examination of a molecular model.

The three ether bonds at C(7) decrease in length in the order C(7)–O(1) > C(7)–O(2) > C(7)–O(9). Although the differences in bond length are small, it is interesting to note that the order of decreasing bond length is the same as the expected order of increasing basicity of the three oxygen atoms: O(1) < O(2) < O(9).

Both C(7)–C(8) and C(10)–C(11) have bond distances similar to those found for the C-methyl bonds in the three acetyl groups. It is difficult to predict an expected value for the C(7)–C(8) distance, but the C(10)–C(11) distance seems shorter than would be expected.

The crystals used in this investigation were of the diastereoisomer which dominates in syntheses of the orthoester, and which has a p.m.r. C(8) methyl singlet at δ 1·71 p.p.m. This isomer has the (*S*)-configuration

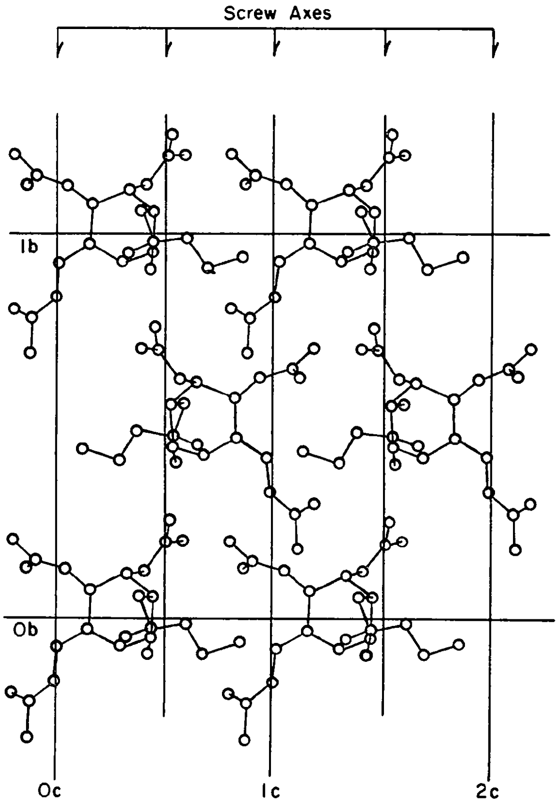

Fig. 3. Unit cells in the *bc* plane viewed from the −**a** direction. Alternate horizontal rows are offset above and below the the plane of the drawing.

Table 4. *Torsion angles* (°)

Ring	Angle	(I) (X-ray)	(I) (p.m.r.)	$^3S_5$[a,b]	$^4C_1$[a]
Pyranose	O(5)–C(1)–C(2)–C(3)	−15·9	—	−33	56·0[c]
	C(1)–C(2)–C(3)–C(4)	42·0	—	71	−53·2[c]
	C(2)–C(3)–C(4)–C(5)	−12·9	—	−33	53·0[c]
	C(3)–C(4)–C(5)–O(5)	−40·2	—	−33	−55·4[c]
	C(4)–C(5)–O(5)–C(1)	72·3	—	71	61·1[c]
	C(5)–O(5)–C(1)–C(2)	−42·0	—	−33	−62·2[c]
	H(1)–C(1)–C(2)–H(2)[d]	10	36 (139)[e]	33	60[b]
	H(2)–C(2)–C(3)–H(3)[d]	57	52 (125)[e]	49	180[b]
	H(3)–C(3)–C(4)–H(4)[d]	95	125 (52)[e]	87	180[b]
	H(4)–C(4)–C(5)–H(5)[d]	168	173[e]	153	180[b]
Dioxolane	O(1)–C(1)–C(2)–O(2)	−16·7			
	C(1)–C(2)–O(2)–C(7)	31·0			
	C(2)–O(2)–C(7)–O(1)	−33·3			
	O(2)–C(7)–O(1)–C(1)	23·0			
	C(7)–O(1)–C(1)–C(2)	3·8			

(*a*) Conformational descriptor from Hough & Richardson (1967). (*b*) Calculated from substituent dihedral angles given by Hough & Richardson (1967) which are based on idealized cyclohexane geometry. (*c*) Average torsion angles for the $^4C_1$ conformation of α-D-glucopyranose derivatives (Arnott & Scott, 1972). (*d*) Absolute values. (*e*) The figures in parentheses are the alternative values calculated from the Karplus (1963) equation. Only one solution of the equation is possible for the value of $J_{4,5}$.

at C(7) (*i.e.*, I) in which the ethoxy group is *trans* or *exo* to the glucopyranose ring (Fig. 2). Obviously then, the minor isomer, with the C(8) methyl singlet at δ 1·56 p.p.m. ($CDCl_3$), has the (*R*)-configuration at C(7). This confirms, on an *absolute* basis, the conclusion based on earlier p.m.r. studies of glucopyranose 1,2-(alkyl orthoacetates) (Lemieux & Morgan, 1965), that the diastereomer for which the C(8) methyl protons resonate at lower field, has the configuration in which the alkoxy group is *exo* to the pyranose ring.

The conformation of the dioxolane ring, defined by the ring torsion angles in Table 4, is best described as being of the envelope type ($E_{O(2)}$), with four atoms essentially planar, and O(2) offset 0·46 Å toward the glucose side of the plane. The fact that C(2), C(1), O(1), and C(7) are nearly coplanar is indicated by the small (3·8°) C(7)–O(1)–C(1)–C(2) torsion angle. The plane of the four atoms is described by equation (5), where X', Y, and Z' refer to the set of orthogonal axes *a*, *b*, and *c**, and are coordinates in Å.

$$-0{\cdot}0021X'+0{\cdot}0681Y-0{\cdot}9977Z'=3{\cdot}6761\,. \qquad (5)$$

Deviations of the atoms from the mean plane were: C(7), −0·019; O(1), 0·014; C(1), −0·026; and C(2), 0·016 Å.

Molecular packing

The bicyclic ring structure of the orthoester has five pendant groups, each of which terminates in a methyl group, representing the extremities of the molecule. In the crystal structure the pendant groups of one molecule overlap and lie between pendant groups from other molecules (Fig. 3). Thus, the intermolecular interactions of the pendant groups, particularly the methyl groups, are the principal means by which the crystal structure is bound together. There is no hydrogen bonding in the structure.

P.m.r. analysis

The p.m.r. coupling constants, $J_{1,2}$ 5·2, $J_{2,3}$ 2·9, $J_{3,4}$ 2·9, $J_{4,5}$ 9·1, and $J_{2,4}$ 1·0 Hz ($CDCl_3$) obtained by first-order analysis of 60 MHz spectra are essentially the same as those obtained for the orthoester in benzene-d_6 at 100 MHz by Dick, Weisleder & Hodge (1972), who also showed that $J_{2,4}$ is positive. The refined Karplus (1963) equation, as employed by Coxon (1968, 1970), was used to calculate approximate vicinal proton dihedral angles* for the orthoester in solution. However, because of the nature of the equation, except for $J_{4,5}$, two dihedral angles, one acute and one obtuse, are permissible solutions of the equation for each vicinal proton coupling constant (Table 4). The question naturally arises as to which of the two angles correctly describes the conformation of the orthoester in solution.

The H(1)–H(2) dihedral angle must be acute because of the fused pyranose–dioxolane ring system. However, the actual dihedral angle in solution is probably less than the 36° (Table 4) indicated by p.m.r. analysis since the electronegative oxygen atoms bonded to C(1) and C(2) would be expected to decrease $J_{1,2}$ (Jackman & Sternhell, 1969; Inch, 1972) with an attendant increase in the 'apparent' dihedral angle. The large value of $J_{4,5}$ is typical of approximately *trans*-diaxial coupling, thus indicating a large, obtuse H(4)–H(5) dihedral angle.

If $J_{2,3}$ and $J_{3,4}$ of the orthoester are interpreted, respectively, in terms of an acute H(2)–H(3) dihedral angle and an obtuse H(3)–H(4) dihedral angle (Table 4), the conformation of the pyranoid ring agrees reasonably well with that found in the crystal structure, *ca* an $^3S_5$ conformation. In addition, these dihedral angle assignments provide an explanation for the observed long-range coupling between H(2) and H(4). As discussed earlier, the system H(2)–C(2)–C(3)–C(4)–H(4) is essentially planar in the crystal structure, a conformation which, in solution, would promote strong, positive H(2)–H(4) coupling (Coxon, 1970). The sign and magnitude of $J_{2,4}$ (*ca* +1·0 Hz) are consistent with a skew-type conformation in solution, and in which some additional deviation of H(2)–C(2)–C(3)–C(4)–H(4) from the optimal planar ('W') relationship has occurred (Inch, 1972; Barfield & Chakrabarti, 1969). Alternatively, if the H(2)–H(3) and H(3)–H(4) dihedral angles are assumed to be obtuse, a flattened-chair conformation in which H(2) and H(4) approach a 1,3-diaxial relationship would be predicted (Lemieux & Morgan, 1965; Trotter & Fawcett, 1966) and $J_{2,4}$, if observed, would be expected to be negative (Barlow, Bishop, Carey, Guthrie, Jensen & Lewis, 1968; Barfield & Chakrabarti, 1969; Inch, 1972), rather than positive.

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* The vicinal proton dihedral angles are the same as the absolute values of the ring hydrogen atom torsion angles (Table 4), H(1)–H(2) dihedral angle ≡ |H(1)–C(1)–C(2)–H(2)|, *etc.*

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Crystal and Molecular Structure of β-1-Phenylsilatrane, $C_{12}H_{17}O_3NSi$

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Two crystalline modifications of 1-phenylsilatrane are reported. The β form is orthorhombic, space group $Pna2_1$, with $a = 15{\cdot}855$, $b = 6{\cdot}648$, $c = 11{\cdot}635$ Å. The γ form is monoclinic, space group $P2_1/n$. The structure of the β form was determined by direct methods with phases generated from the partially known structure and recycled into the tangent formula. The structure was refined to $R = 0{\cdot}076$ for 1103 observed reflexions and 0·079 for all 1134 reflexions. The Si–N bond length is 2·156 (4), the Si–C 1·908 (5) Å. The mean Si–O bond distance is 1·657 Å. The N–Si–C angle is 177·0°, the average N–Si–O, C–Si–O and O–Si–O angles are 83·3°, 96·8° and 118·6°. The carbon atoms α to the nitrogen are bent out of the plane of the five-membered rings.

Introduction

The crystal structure of α-1-phenylsilatrane, $C_6H_5\overset{\downarrow}{Si}(OCH_2CH_2)_3N$, was determined by Turley & Boer (1968). The structure is disordered. By recrystallization from acetone we could isolate two other crystalline modifications, called the β and γ forms. These can be easily separated by their shapes. Infrared spectra of the three modifications in KBr pellets were recorded. While the spectra of the α and γ forms were similar, and practically identical with the spectrum published by Voronkov (1966), the spectrum of the β form showed large differences.* In the present paper we give an account of the structure of the β form.

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* Unpublished results.