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CONFORMATION OF 3,4,6-TRI-*O*-ACETYL-1,2-DIDEOXY-α-D-GLUCOPYRANO-[2,1-*d*]-2-OXAZOLINES

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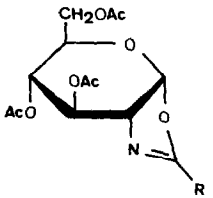
ABSTRACT

The crystal and molecular structure of 2-phenyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano)-[2,1-*d*]-2-oxazoline (**2**) has been determined. The compound crystallises in the space group $P2_12_12$ with lattice constants 13.4160(3), 37.4931(14), and 7.7886(1) Å, and Z = 8. Direct methods were used in the solution. Least squares refined the model with 3213 observed (with 2σ) reflections down to an R value of 0.053 and R_ω 0.060. The pyranoid rings have slightly different conformations, being between skew $^OS_2$ and diplanar $D^{O,4}$. The conformations of **2** and 2-methyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano)-[2,1-*d*]-2-oxazoline in solution have also been investigated by ^{1}H-n.m.r. spectroscopy. The computed best values of the coupling constants have been used with several Karplus-type equations and have been interpreted in terms of a skew $^OS_2$ major conformation of the pyranoid ring in each compound.

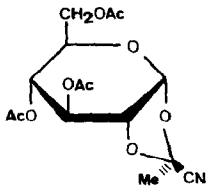
INTRODUCTION

The conformation of the pyranoid ring of 2-methyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano)-[2,1-*d*-]-oxazoline (**1**) in solution has been previously studied by ^{1}H-n.m.r. spectroscopy[1,2], and both a modified skew[1] ($^OS_2$) and a distorted half-chair[2] ($^4H_5$) conformation have been proposed on the basis of the values



1 R = Me

2 R = Ph



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0008-6215/84/$ 03.00

of vicinal couplings. We have demonstrated that the conformation of the pyranoid ring of the closely related compound 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-cyanoethylidene)-α-D-glucopyranose (**3**), both in the crystalline solid[3] and in solution[4], can be described as modified $^{O}S_{2}$, and similar skew conformations have been found for other acetylated 1,2-*O*-alkylidene-α-D-hexopyranoses[5,6]. We now report the molecular structure of crystalline 2-phenyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano)-[2,1-*d*]-oxazoline (**2**) and the analysis of the 360-MHz ^{1}H-n.m.r. spectra of **1** and **2**. As in previous communications[4,5,7], several Karplus-type equations have been used to estimate approximately the vicinal-proton torsion angles and to determine the major conformation in solution.

EXPERIMENTAL

Materials. — Compounds **1** and **2** were prepared as reported in the literature[2,13]. Compound **2** crystallised from ether and had m.p. 78–80°.

X-Ray studies. — Crystal and experimental data, together with characteristics

TABLE I

CRYSTAL STRUCTURE PARAMETERS FOR **2** AT ROOM TEMPERATURE

Crystal data	
Formula	$C_{19}H_{21}NO_8$
Crystal colour, habit, and size	Transparent, colourless, parallepipedic 0.48 × 0.16 × 0.13 mm
Symmetry	Orthorhombic $P2_12_12$
Unit-cell dimensions (Å)	$a = 13.4160\ (3)$, $b = 37.4931\ (14)$, $c = 7.886\ (1)$
Packing parameters: V(Å^3), Z, DC(Mg m^{-3}), M_r	3917.8, 8, 1.327, 391.38
Experimental	
Technique	Four-circle Philips PW 1100 diffractometer, bisecting geometry
Collection mode	$\omega/2\theta$; θ(Max.-Cu) = 65°
No. of data collected	3804 independent 3213 observed; 2σ (I) criterion.
Stability from two standards	Monitored every 90 min; no variation
Solution and refinement	
Solution mode	MULTAN[14]; 6 highest E's per non-H atoms
Refinement mode	Least squares on F's, observed data only, 15 blocks matrix, H's isotropic Final max. shift/error = 0.46.
ω-Scheme	Empirical, to give no trends in $\langle\omega\Delta^2\rangle$ *vs.* $\langle F_0\rangle$ or $\langle\sin\theta/\lambda\rangle$[a].
Max. thermal value	U22 (07) = 0.35 (1), Å^2
Difference synthesis	Final noise ±0.43 eÅ^{-3}
Final R and R_ω (obs. reflections)	0.053, 0.060
Atomic scattering factors	International Tables[15]
Computing	X-RAY 70 System[16] on UNIVAC 1100/80

[a]The weights were chosen as $\omega = k/[f(F_0)]^2[g(\sin\theta/\lambda)]$, first fitting ΔF *vs.* F_0, to obtain $f(F_0)$, and then $\Delta^2F/f^2(F_0)$ *vs.* $\sin\theta/\lambda$, to obtain the g-function; k is a scale factor to assure $\langle\omega\Delta^2\rangle \sim 1$.

TABLE II

FINAL FRACTIONAL ATOMIC CO-ORDINATES AND THERMAL PARAMETERS

Atom	x/a	y/b	z/c	$U_{eq} \times 10^3$
C-1	0.66855(29)	0.01432(11)	0.00790(60)	41(1)
O-1	0.60714(20)	0.02472(7)	−0.13768(36)	42(1)
C-2	0.60962(30)	0.02714(11)	0.16274(53)	42(1)
N-2	0.52679(23)	0.04839(9)	0.09219(45)	42(1)
C-3	0.67401(30)	0.04862(11)	0.28427(54)	37(1)
O-3	0.73575(21)	0.02218(7)	0.36796(35)	42(1)
C-4	0.73866(29)	0.07703(9)	0.19860(52)	34(1)
O-4	0.67725(20)	0.10892(7)	0.19280(38)	43(1)
C-5	0.76702(27)	0.06713(10)	0.01454(51)	34(1)
O-5	0.76412(17)	0.02905(6)	−0.00954(36)	38(1)
C-6	0.87060(31)	0.07881(12)	−0.03622(63)	43(1)
O-6	0.94129(19)	0.06176(8)	0.07764(38)	45(1)
C-7	1.03162(42)	0.05613(16)	0.02099(69)	70(2)
O-7	1.05818(44)	0.06690(26)	−0.11689(86)	187(4)
C-8	1.09987(50)	0.03954(21)	0.14588(106)	80(2)
O-8	0.80474(29)	0.14134(10)	0.29073(83)	99(2)
C-9	0.72082(38)	0.13969(11)	0.24557(70)	56(2)
O-9	0.76556(26)	0.06070(8)	0.58304(39)	55(1)
C-10	0.64728(62)	0.16965(16)	0.24017(105)	78(2)
C-11	0.77681(31)	0.03140(11)	0.52189(54)	45(1)
C-12	0.83439(80)	0.00147(22)	0.59417(96)	76(2)
C-13	0.53166(26)	0.04483(10)	−0.07173(55)	37(1)
C-14	0.46240(28)	0.06034(11)	−0.19716(51)	37(1)
C-15	0.47531(37)	0.05390(14)	−0.37175(64)	53(2)
C-16	0.41243(37)	0.06942(15)	−0.49061(74)	62(2)
C-17	0.33585(41)	0.09087(16)	−0.43668(76)	65(2)
C-18	0.32013(40)	0.09666(15)	−0.26380(77)	65(2)
C-19	0.38456(38)	0.08175(13)	−0.14397(68)	52(2)
C-1′	−0.00379(38)	0.22245(13)	−0.07738(63)	53(1)
O-1′	−0.10791(23)	0.22153(7)	−0.13050(44)	52(1)
C-2′	0.03525(35)	0.18545(12)	−0.12594(65)	49(1)
N-2′	−0.05489(25)	0.16477(9)	−0.16927(45)	43(1)
C-3′	0.09672(29)	0.16740(12)	0.01247(59)	45(1)
O-3′	0.19628(20)	0.18186(8)	−0.00716(44)	55(1)
C-4′	0.06056(32)	0.17388(11)	0.19802(58)	40(1)
O-4′	0.02951(20)	0.14049(7)	0.27029(38)	43(1)
C-5′	−0.02555(31)	0.19984(11)	0.20590(56)	43(1)
O-5′	0.00127(25)	0.22981(7)	0.09924(40)	52(1)
C-6′	−0.04102(48)	0.21339(17)	0.38620(78)	63(2)
O-6′	−0.12662(31)	0.23572(12)	0.38565(56)	86(2)
C-7′	−0.12311(59)	0.26566(17)	0.47910(85)	80(2)
O-7′	−0.05372(48)	0.27376(12)	0.56757(77)	102(2)
C-8′	−0.21930(95)	0.28567(31)	0.47432(142)	144(5)
O-8′	0.12120(25)	0.15120(10)	0.50730(46)	64(1)
C-9′	0.06358(34)	0.13270(12)	0.43129(62)	49(1)
O-9′	0.25624(27)	0.13618(11)	0.14349(55)	79(1)
C-10′	0.01534(60)	0.09963(16)	0.49705(95)	69(2)
C-11′	0.26966(36)	0.16315(17)	0.06673(75)	70(2)
C-12′	0.36882(46)	0.18238(31)	0.04211(131)	104(4)

TABLE II *(continued)*

Atom	x/a	y/b	z/c	$U_{eq} \times 10^3$
C-13′	−0.12654(32)	0.18661(10)	−0.17374(53)	41(1)
C-14′	−0.23059(30)	0.17857(10)	−0.21775(51)	39(1)
C-15′	−0.30678(36)	0.20345(12)	−0.19579(65)	52(1)
C-16′	−0.40344(38)	0.19451(14)	−0.23601(74)	61(2)
C-17′	−0.42555(36)	0.16079(14)	−0.29676(71)	56(2)
C-18′	−0.35060(34)	0.13591(12)	−0.31954(64)	50(1)
C-19′	−0.25277(33)	0.14517(11)	−0.28244(60)	45(1)
H-1	0.6857(29)	−0.0104(12)	−0.0089(56)	16(10)
H-2	0.5807(30)	0.0056(11)	0.2275(51)	11(10)
H-3	0.6355(33)	0.0584(11)	0.3581(60)	6(11)
H-4	0.7963(31)	0.0793(10)	0.2606(51)	0(9)
H-5	0.7198(29)	0.0797(10)	−0.0776(54)	4(9)
H-6A	0.8770(32)	0.1042(13)	−0.0114(60)	21(11)
H-6B	0.8821(44)	0.0720(15)	−0.1413(90)	37(17)
H-8A	1.0521(73)	0.0345(24)	0.2355(128)	101(32)
H-8B	1.1479(70)	0.0607(22)	0.1643(112)	110(27)
H-8C	1.1479(83)	0.0333(26)	0.1020(140)	94(37)
H-10A	0.5927(93)	0.1643(33)	0.3084(178)	144(51)
H-10B	0.6279(64)	0.1762(23)	0.1362(128)	82(29)
H-10C	0.6814(77)	0.1897(29)	0.2644(141)	116(38)
H-12A	0.8671(52)	−0.0113(20)	0.5394(92)	53(22)
H-12B	0.7975(98)	−0.0099(38)	0.6325(187)	120(74)
H-12C	0.8725(61)	0.0077(21)	0.6834(118)	71(25)
H-15	0.5285(43)	0.0413(14)	−0.4041(70)	37(14)
H-16	0.4247(49)	0.0669(17)	−0.6085(101)	50(20)
H-17	0.3040(39)	0.1043(13)	−0.5166(71)	26(13)
H-18	0.2601(46)	0.1095(15)	−0.2307(77)	50(16)
H-19	0.3770(44)	0.0864(15)	−0.0309(89)	46(16)
H-1′	0.0249(31)	0.2405(12)	−0.1270(55)	8(10)
H-2′	0 0739(38)	0.1873(13)	−0.2081(71)	22(13)
H-3′	0.0974(29)	0.1434(12)	−0.0077(55)	16(10)
H-4′	0 1097(35)	0.1801(11)	0.2534(59)	12(12)
H-5′	−0.0933(28)	0.1890(10)	0.1638(50)	18(9)
H-6′A	0.0041(36)	0.2252(12)	0.4126(58)	6(12)
H-6′B	−0.0506(43)	0.1916(16)	0.4715(82)	50(17)
H-8′A	−0 2677(51)	0.2717(19)	0.4178(97)	40(23)
H-8′B	−0.2534(82)	0.2859(31)	0.3423(153)	116(43)
H-8′C	−0.2051(69)	0.3136(23)	0.5230(130)	156(33)
H-10′A	0.0111(95)	0.0976(31)	0.6060(166)	128(44)
H-10′B	0.0622(55)	0.0842(19)	0.5223(97)	54(20)
H-10′C	−0.0519(86)	0.0960(29)	0.4683(154)	212(46)
H-12′A	0.3743(66)	0.2014(23)	0.1395(129)	110(30)
H-12′B	0.3851(90)	0.1743(32)	−0.0381(159)	103(48)
H-12′C	0.4139(88)	0.1627(29)	0.0828(156)	130(40)
H-15′	−0.2928(39)	0.2260(16)	−0.1613(71)	32(15)
H-16′	−0.4552(38)	0.2094(13)	−0.2272(64)	18(12)
H-17′	−0.4832(44)	0.1539(13)	−0.3295(68)	33(14)
H-18′	−0.3612(39)	0.1123(14)	−0.3716(71)	24(14)
H-19′	−0.2025(36)	0.1296(13)	−0.3010(63)	30(12)

TABLE III

BOND DISTANCES (Å)[a]

Bond	*Molecule*	
	2a	**2b**
C-1–C-2	1.520(6)	1.530(7)
C-2–C-3	1.514(6)	1.517(7)
C-3–C-4	1.527(6)	1.544(6)
C-4–C-5	1.529(6)	1.512(6)
C-5–O-5	1.441(4)	1.443(5)
C-1–O-5	1.403(5)	1.405(6)
C-1–O-1	1.455(5)	1.457(6)
C-2–N-2	1.474(5)	1.476(6)
C-13–N-2	1.285(5)	1.263(5)
C-13–O-1	1.363(5)	1.375(5)
C-5–C-6	1.510(6)	1.508(8)
C-3–O-3	1.447(5)	1.450(5)
C-4–O-4	1.453(4)	1.434(5)
C-6–O-6	1.447(5)	1.421(7)
C-7–O-6	1.307(6)	1.339(8)
C-9–O-4	1.357(5)	1.366(6)
C-11–O-3	1.364(5)	1.339(6)
C-7–O-7	1.201(9)	1.197(10)
C-9–O-8	1.181(7)	1.200(6)
C-11–O-9	1.207(5)	1.188(8)
C-7–C-8	1.474(10)	1.493(15)
C-9–C-10	1.496(8)	1.490(8)
C-11–C-12	1.474(10)	1.525(9)

[a]E.s.d. values given in parenthesis.

of the solution and refinement processes, are presented in Table I. All H-atoms were located by a difference synthesis. The final fractional co-ordinates are given in Table II*, bond distances and angles are given in Tables III and IV, respectively, and the main torsion angles of the pyranoid and oxazoline rings are shown in Table V.

^{1}H-N.m.r. spectroscopy. — The spectra of **1** and **2** were recorded for solutions in $CDCl_3$ (internal Me_4Si), using a Bruker WP-360 spectrometer operating at 360 MHz. Analyses were performed by an ASPECT 2000 data system, using a PANIC program. The experimental and calculated spectra from the resulting best values matched satisfactorily.

RESULTS AND DISCUSSION

Two crystallographically independent molecules (**2a** and **2b**) are present in

*Lists of structure factors and thermal parameters have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/297/*Carbohydr. Res.*, 135 (1984) 1 -11.

TABLE IV

MAIN BOND ANGLES[a]

Angle	*Molecule*		*Angle*	*Molecule*	
	2a	**2b**		**2a**	**2b**
C-4–C-5–O-5	110.9(3)	106.7(3)	C-2–C-1–O-5	115.3(4)	113.8(4)
C-1–O-5–C-5	113.7(3)	113.5(3)	C-1–C-2–C-3	111.6(3)	114.5(4)
C-2–C-3–C-4	115.0(3)	115.1(4)	C-3–C-4–C-5	112.4(3)	112.3(4)
C-1–C-2–N-2	105.5(3)	104.6(4)	C-2–C-1–O-1	103.8(3)	103.7(4)
C-2–C-2–C-13	106.0(3)	106.8(3)	C-1–O-1–C-13	106.0(3)	105.5(3)
O-1–C-13–N-2	118.0(3)	118.2(4)			
O-5–C-5–C-6	106.2(3)	108.0(4)	C-1–C-5–C-6	113.8(3)	111.1(4)
C-5–C-4–O-4	108.2(3)	108.9(3)	C-3–C-4–O-4	105.4(3)	108.7(3)
C-4–C-3–O-3	110.5(3)	109.2(3)	C-2–C-3–O-3	104 1(3)	105.0(3)
O-5–C-1–O-1	109.7(3)	109.2(4)	C-3–C-2–N-2	112.1(3)	112.0(4)
C-5–C-6–O-6	108.3(3)	107.9(5)	C-6–O-6–C-7	118.2(4)	117.6(5)
C-4–O-4–C-9	116.5(3)	116.7(3)	C-3–O-3–C-11	117.0(3)	115.9(4)
N-2–C-13–C-14	126.0(4)	126.6(4)	O-1–C-13–C-14	116.0(3)	115.2(3)
C-13–C-14–C-15	120.2(4)	122.1(4)	C-13–C-14–O-19	120 6(4)	118.4(4)
C-19–C-14–C-15	119.2(4)	118.4(4)			
O-6–C-7–O-7	121.5(6)	123.5(6)	O-4–C-9–O-8	123 1(4)	123.2(4)
O-3–C-11–O-9	121.8(4)	123.4(5)	O-6–C-7–C-8	114.9(5)	112.2(7)
O-4–C-9–C-10	110.2(5)	110.4(4)	O-3–C-11–C-12	110.8(4)	109.9(6)
O-7–C-7–C-8	123.2(6)	124.0(7)	O-8–C-9–C-10	126.7(5)	126.4(5)

[a]E.s.d. values given in parenthesis.

TABLE V

EXPERIMENTAL TORSION ANGLES (°) AND CONFORMATIONAL PARAMETERS

Angles and parameters	*Molecule*		
	2a	**2b**	**3**
	Pyranoid ring		
C-2–C-1–O-5–C-5	−46.0(4)	−40.4(5)	−39.8(4)
C-1–O-5–C-5–C-4	+64.7(4)	+73.9(4)	+69.7(4)
O-5–C-5–C-4–C-3	−24.6(4)	−47.1(4)	−38.7(5)
C-5–C-4–C-3–C-2	−28.8(5)	−4.7(5)	−14.9(6)
C-4–C-3–C-2–C-1	+46.9(5)	+37.0(5)	+42.4(6)
C-3–C-2–C-1–O-5	−10.0(5)	−15 5(6)	−16.5(5)
	Oxazoline ring		
N-2–C-2–C-1–O-1	−8.0(4)	−11.1(5)	
C-2–C-1–O-1–C-13	+7.2(4)	+9.2(4)	
C-1–O-1–C-13–N-2	−3.9(5)	−3.9(5)	
O-1–C-13–N-2–C-1	−1.5(5)	−3.7(5)	
C-13–N-2–C-2–C-1	6.0(4)	9.2(5)	

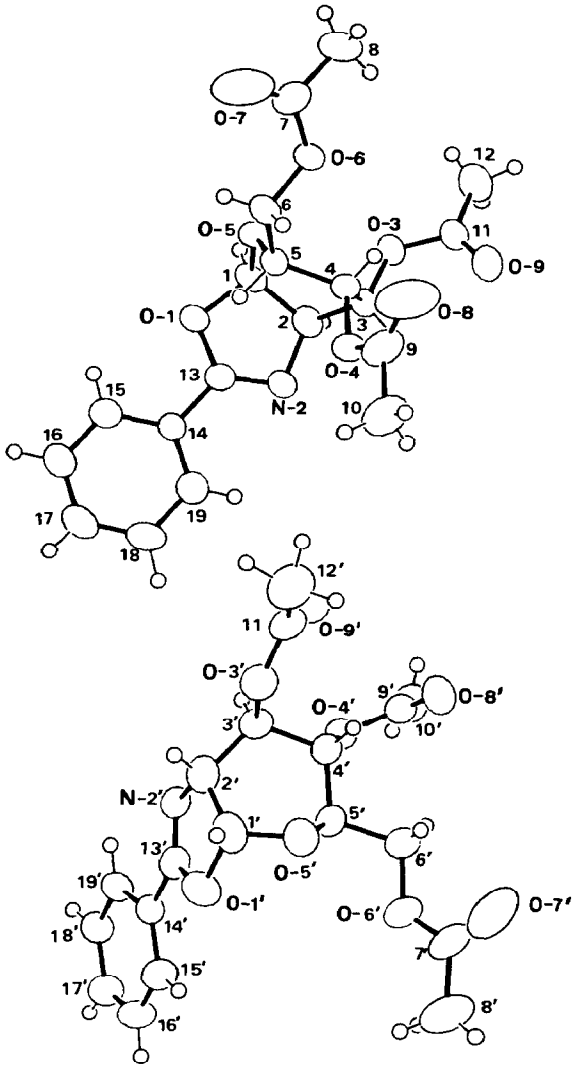


Fig. 1. An ORTEP view of the two independent molecules, showing the atomic numbering.

the crystalline structure of **2** (Fig. 1). The main diffeences between these appear at the double bond C-13–N-2 and at the bonds C-6–O-6, O-6–C-7, C-4–O-4, C-11–C-12, and C-11–O-3, and at the angles around C-5, at C-6 and O-3, the internal angle C-1–C-2–C-3, and the exocyclic angle C-3–C-4–O-4. Among the C–O distances, with an average of 1.426 Å, is the sequence C-1–O-5<C-1–O-1~C–O~C-5–O-5. The angles around C-13 reflect the double bond's diminishing of the opposite angle and enlarging of the endocyclic ring angle. The geometry of the aromatic ring is as expected.

The two pyranoid rings have slightly different conformations, both being in

TABLE VI

^{1}H-N M R DATA FOR **1** AND **2** AT 360 MHz

Parameter[a]	*Compound*		
	1	**2**	**3**
ν_1	5.973	6.184	5.803
ν_2	4.140	4.391	4.390
ν_3	5.269	5.431	5.213
ν_4	4.935	4.982	4.916
ν_5	3.611	3.673	3.906
ν_{6a}	4.184	4.184	4.193
ν_{6b}	4.173	4.166	4.193
$J_{1,2}$	7.4	7.4	5.2
$J_{1,3}$	−0.3	−0.3	−0.4
$J_{1,5}$	−0.6	−0.7	−0.7
$J_{2,3}$	2.7	2.6	3.0
$J_{2,4}$	1.3	1.2	0.9
$J_{3,4}$	2.1	2.1	2.8
$J_{4,5}$	9.2	9.1	9.5
$J_{5,6a}$	3.0	3.0	5.7
$J_{5,6b}$	5.8	5.8	2.8
$J_{6a,6b}$	−12.3	−12.3	−12.1

[a] ν (δ) and J (Hz).

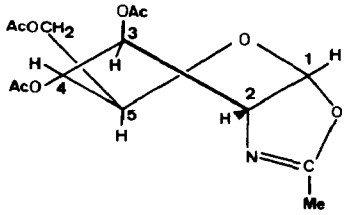
TABLE VII

VICINAL-PROTON TORSION ANGLE (°) FOR **1–3** DEDUCED FROM ^{1}H-N.M.R DATA

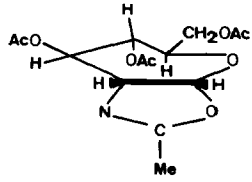
Compound	*Equation (ref.)*	$\phi_{1,2}$	$\phi_{2,3}$	$\phi_{3,4}$	$\phi_{4,5}$
1	9	—	−67(−123)	124(74)	−166
	10	27	66	69	
	11	18	53(123)	119(57)	177
	12	26	60(126)	120(65)	
2	9	—	−67(−122)	124(74)	−164
	10	27	66	69	
	11	18	54(123)	119(57)	174
	12	26	61(125)	120(65)	
3	9	−17	−66(−130)	121(64)	−170
	10	5	65	65	
	11	36	51(125)	124(52)	
	12	41	58(129)	127(60)	

between a skew form $^{O}S_2$ (**4**) with a two-fold axis through C-1 and C-4, and a diplanar form $D^{O,4}$, flattened at C-1–C-2 and C-3–C-4 with the two-fold axis through the mid points of O-5–C-5 and C-2–C-3. The five-membered rings also have slightly different conformations, near $_1T^2$ with the two-fold axis through C-2, and in between $_1T^2$ and E_1 with the mirror plane through C-1. The overall puckering in both rings is quite low[8].

The 360-MHz ^{1}H-n.m.r. spectra of compounds **1** and **2** were recorded, and



4 ($^{O}S_2$)



5 ($^{4}H_5$)

simulated using a LAOCOON/3 computer program. The computed best values of the chemical shifts and coupling constants, compared to those calculated[4] for the nitrile **3**, are given in Table VI. The vicinal-proton torsion angles of the pyranoid rings calculated from the vicinal coupling constants, using the general equation of Altona *et al.*[9], the equation of Forrest[10], and the equations parametrised for carbohydrates proposed by Coxon[11] and Vliegenthart *et al.*[12], are shown in Table VII, and the same angles determined by X-ray diffraction are given in Table VIII.

The best values of vicinal couplings given in Table VI for **1** are similar to those previously determined on the basis of first-order analysis[1,2] and those found[4] for the nitrile **3**. We have shown[4,5] that the major conformation of **3** and other 3,4,6-tri-*O*-acetyl-1,2-*O*-alkylidene-α-D-glucopyranose derivatives in solution can be better described as $^{O}S_2$, which is similar to that found for this compound in the crystalline solid, the main argument being the existence of a large and positive long-range coupling constant between H-2 and H-4 and n.O.e. experiments which indicated the proximity of the *endo*-methyl group of **3** to H-5 but not to H-3. Nashed *et al.*[1] concluded from the vicinal couplings that $\phi_{2,3}$, $\phi_{3,4}$, and $\phi_{4,5}$ for **1** should be in the ranges 50–60°, 110–120°, and 160–180°, respectively, and that a modified $^{O}S_2$ conformation is the only one in which these values could be accommodated, although $\phi_{1,2}$ should be smaller than in the "theoretical" skew form. However, Srivastava[2] argued that the value for $\phi_{2,3}$ of 50–60° "appears to be in question as this would require a $\phi_{3,4}$ dihedral angle equal to 80° and not 110–120°". Alternatively, "if $\phi_{3,4}$ were increased to give the $\phi_{3,4}$ angle of 110–120°, $\phi_{2,3}$ would

TABLE VIII

VICINAL-PROTON TORSION ANGLES (°) DETERMINED BY THE X-RAY METHOD

Angle	*Compound*		
	2a	**2b**	**3**[4]
$\phi_{1,2}$	−11(4)	−10(5)	−18(5)
$\phi_{2,3}$	−69(4)	−82(5)	−67(6)
$\phi_{3,4}$	91(4)	107(4)	95(4)
$\phi_{4,5}$	−143(4)	−165(4)	−148(5)
$\phi_{5,6a}$	70(4)	−167(4)	50(6)
$\phi_{5,6b}$	−59(5)	70(4)	−74(6)

approach ~75° and again would result in a lower $J_{2,3}$ value (<0.5 Hz) than that observed". Srivastava concluded that a distorted $^4H_5$ conformation **5** of the pyranoid ring flattened at C-2 and C-4 gives a better fit of the observed n.m.r. data. As indicated by the data in Table VIII, all equations account for a $\phi_{2,3}$ angle in the range 50–70°, with the equation of Altona *et al.*[9], which takes into account the electronegativity and orientation of substituents, giving the highest values. Values for $\phi_{3,4}$ between 116 and 124° were found with all equations, with the exception of that of Forrest[10] which can be used only for *gauche* coupling.

These values of $\phi_{2,3}$ and $\phi_{3,4}$ seem to indicate that the major solution conformation of **1** and **2** may be described as skew $^OS_2$, as previously reported by Nashed *et al.*[1] and demonstrated[4,5] for **3** and other derivatives. Furthermore, the conformation of the pyranoid ring in crystalline **2**, although slightly different for the two crystallographically independent molecules (**2a** and **2b**), can also be described as skew $^OS_2$. Although the vicinal-proton torsion angles determined from X-ray crystallographic data should not be directly compared with the values obtained from n.m.r. studies, the order of magnitude of the angles reported in Table VIII agrees reasonably with those in Table VII, indicating that $^OS_2$ is the major conformation of **2** (and hence **1**) in solution instead of $^4H_5$ as proposed by Srivastava[2]. Furthermore, the large and positive* $J_{2,4}$ value is also indicative of a planar arrangement of H-2,4, which is present in the $^OS_2$ conformation but not in the $^4H_5$ form.

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*The sign of this long-range constant has been determined using the spin-decoupling method[17]

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