Tabelle 2. *Bindungsabstände* (Å) *und -winkel* (°)

Standardabweichung der letzten Stelle in Klammern.

O(1)—C(5)	1,254 (7)	C(11)—C(24)	1,429 (7)
O(2)—C(6)	1,267 (7)	C(12)—C(25)	1,466 (8)
C(1)—C(2)	1,439 (7)	C(13)—C(14)	1,388 (8)
C(1)—C(18)	1,450 (6)	C(13)—C(25)	1,444 (7)
C(2)—C(3)	1,386 (8)	C(14)—C(15)	1,463 (7)
C(3)—C(4)	1,376 (7)	C(15)—C(16)	1,382 (7)
C(4)—C(17)	1,432 (7)	C(16)—C(26)	1,455 (7)
C(5)—C(6)	1,475 (8)	C(17)—C(18)	1,394 (7)
C(5)—C(17)	1,458 (7)	C(18)—C(19)	1,485 (7)
C(6)—C(20)	1,448 (7)	C(19)—C(20)	1,386 (7)
C(7)—C(8)	1,357 (7)	C(19)—C(22)	1,451 (7)
C(7)—C(20)	1,431 (7)	C(21)—C(22)	1,431 (7)
C(8)—C(21)	1,397 (7)	C(22)—C(23)	1,458 (7)
C(9)—C(10)	1,332 (7)	C(23)—C(24)	1,427 (7)
C(9)—C(21)	1,463 (7)	C(23)—C(26)	1,446 (7)
C(10)—C(24)	1,458 (8)	C(25)—C(26)	1,409 (6)
C(11)—C(12)	1,348 (7)		

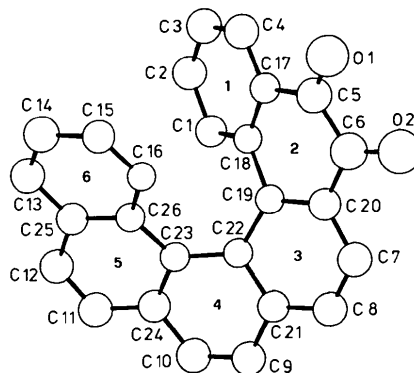|			
C(2)—C(1)—C(18)	118,5 (5)	C(17)—C(18)—C(19)	121,5 (6)
C(1)—C(2)—C(3)	119,0 (5)	C(18)—C(19)—C(20)	119,5 (6)
C(2)—C(3)—C(4)	124,5 (6)	C(18)—C(19)—C(22)	122,8 (6)
C(3)—C(4)—C(17)	116,3 (6)	C(20)—C(19)—C(22)	117,7 (5)
O(1)—C(5)—C(6)	118,8 (6)	C(6)—C(20)—C(7)	121,5 (6)
O(1)—C(5)—C(17)	122,9 (6)	C(6)—C(20)—C(19)	116,5 (7)
C(6)—C(5)—C(17)	118,3 (6)	C(7)—C(20)—C(19)	121,9 (6)
O(2)—C(6)—C(5)	119,0 (6)	C(8)—C(21)—C(9)	120,6 (6)
O(2)—C(6)—C(20)	119,8 (7)	C(8)—C(21)—C(22)	120,1 (6)
C(5)—C(6)—C(20)	121,3 (7)	C(9)—C(21)—C(22)	119,4 (6)
C(8)—C(7)—C(20)	118,7 (7)	C(19)—C(22)—C(21)	117,4 (5)
C(7)—C(8)—C(21)	121,6 (6)	C(19)—C(22)—C(23)	125,2 (5)
C(10)—C(9)—C(21)	119,8 (6)	C(21)—C(22)—C(23)	117,4 (6)
C(9)—C(10)—C(24)	122,8 (6)	C(22)—C(23)—C(24)	119,3 (6)
C(12)—C(11)—C(24)	118,8 (6)	C(22)—C(23)—C(26)	125,4 (5)
C(11)—C(12)—C(25)	121,6 (6)	C(24)—C(23)—C(26)	115,2 (6)
C(14)—C(13)—C(25)	118,5 (6)	C(10)—C(24)—C(11)	119,1 (6)
C(13)—C(14)—C(15)	119,8 (6)	C(10)—C(24)—C(23)	117,6 (6)
C(14)—C(15)—C(16)	120,4 (5)	C(11)—C(24)—C(23)	123,2 (6)
C(15)—C(16)—C(26)	121,0 (5)	C(12)—C(25)—C(13)	118,9 (6)
C(4)—C(17)—C(5)	120,1 (6)	C(12)—C(25)—C(26)	118,2 (6)
C(4)—C(17)—C(18)	123,0 (5)	C(13)—C(25)—C(26)	122,9 (6)
C(5)—C(17)—C(18)	116,5 (6)	C(16)—C(26)—C(23)	121,9 (5)
C(1)—C(18)—C(17)	118,2 (6)	C(16)—C(26)—C(25)	116,8 (6)
C(1)—C(18)—C(19)	120,2 (6)	C(23)—C(26)—C(25)	121,3 (5)

Fig. 1. Molekül mit *ORTEP* (Johnson, 1965) (50%) gezeichnet mit Bezeichnung der Atome und Ringe.

atome liegen $-0{,}44$ (1) [O(1)] und 0,34 (1) Å [O(2)] außerhalb der Ringebene. Die Winkel zwischen den Ebenen aufeinander folgender Ringe (1···6) sind 17,1 (3), 11,7 (6), 12,1 (8), 12,5 (10), 9 (2)°.

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Structure of (6*R*)-1,4,7-Trioxaspiro[5.5]undecan-10-one

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Abstract. $C_8H_{12}O_4$, $M_r = 172{\cdot}18$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}819$ (2), $b = 9{\cdot}995$ (2), $c = 12{\cdot}333$ (3) Å, $V = 840{\cdot}6$ (4) Å^3, $D_x = 1{\cdot}360$ Mg m^{-3}, λ(Cu Kα) = 1·5418 Å, $\mu = 0{\cdot}935$ mm^{-1}, $Z = 4$, $F(000) = 368$, room temperature, $R = 0{\cdot}045$ for 648 independent reflections with $I > 2\sigma(I)$. Bond lengths and angles have normal values. The conformation of the molecule results from the occurrence of the anomeric and *exo*-anomeric effect. Both rings have a chair geometry.

Introduction. This work is a continuation of our studies concerning the X-ray crystal structures of pyranosides with one sp^2-hybridized C atom in the ring (Ciunik, Paulsen, Luger, Smiatacz & Myszka, 1989; Smiatacz, Myszka & Ciunik, 1988). Pyranoid rings with the C(sp^2) atom in a vicinal positional with respect to the anomeric center have a chair conformation which seems nonetheless to be flexible. This flexibility is shown by deformations of the chair conformation which are relatively large in some cases compared to the geometry of the pyranoid rings without an exocyclic double bond. The principal aim of this work is to determine the conformation of the title compound, which has a keto group in the opposite position to the ring acetal oxygen.

Experimental. The title compound is one of the intermediate products in the enantiospecific synthesis of (R)-1,4,7-trioxaspiro[5.5]undecane and was obtained by Aamlid, Hough, Richardson & Hendry (1987). Crystal dimensions $0.20 \times 0.15 \times 0.05$ mm, orientation along **a**, DEC MicroPDP11-controlled Stoe-AED diffractometer, Ni-filtered Cu $K\alpha$ radiation. Lattice parameters from 25 reflections ($30 \leq 2\theta \leq 40°$), $\omega/2\theta$ scan, $5 \leq 2\theta \leq 120°$, $0 \leq h \leq 6$, $0 \leq k \leq 11$, $0 \leq l \leq 13$, three standard reflections showed systematic drop in intensity (about 45%) during the X-ray experiment, and the intensities of the measured reflections were rescaled according to the variations of the standards. The total number of independent reflections measured was 712 [$0.0644 \leq (\sin\theta/\lambda) \leq 0.6513$ Å^{-1}], 648 with $I > 2\sigma(I)$ considered observed. No absorption correction. The structure was solved by direct methods and refined (on F) with isotropic and then with anisotropic temperature factors by the full-matrix least-squares method. The H-atom positions were calculated based on the geometry of the molecule (C—H = 0.95 Å). Refinement of all 109 non-H-atom parameters converged with $R = 0.045$, $wR = 0.047$, $S = 0.686$, final $(\Delta/\sigma)_{max} \leq 0.065$, $-0.20 \leq \Delta\rho \leq 0.22$ e Å^{-3}, function minimized $\Sigma w(|F_o| - |F_c|)$, and unit weights. The final atomic parameters are given in Table 1.* All crystallographic computations were performed on a VAX/VMS V4.6 computer using SHELXS86 (Sheldrick, 1986), XTAL2.2 (Hall & Stewart, 1987), with neutral-atom scattering factors and anomalous-dispersion corrections for O atoms included in the program; XTAL versions of ORTEPII (Johnson, 1971) and PUCK2 (Luger & Bülow, 1983) were also used.

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* Lists of structure factors, anisotropic thermal parameters, dihedral angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53999 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional and thermal parameters* ($\times 10^2$) *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

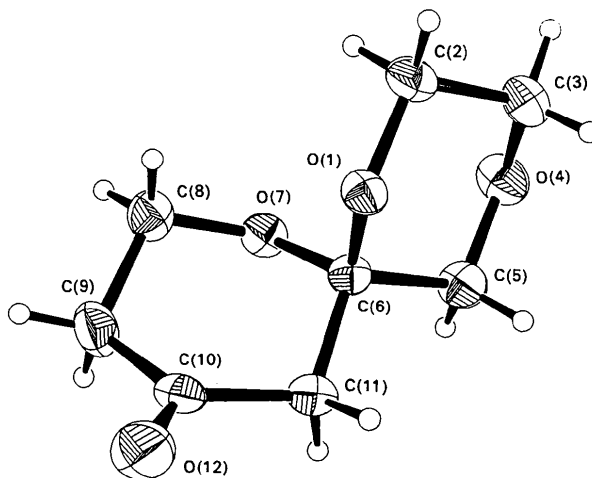|	x	y	z	U_{eq} (Å^2)
O(1)	0.2554 (6)	-0.0827 (3)	0.0199 (2)	4.2 (1)
C(2)	0.3187 (9)	0.0520 (6)	-0.0044 (4)	5.4 (2)
C(3)	0.153 (1)	0.1481 (6)	0.0135 (5)	6.4 (2)
O(4)	0.0833 (7)	0.1423 (4)	0.1239 (3)	6.3 (2)
C(5)	0.0189 (9)	0.0083 (6)	0.1468 (4)	5.2 (2)
C(6)	0.1791 (8)	-0.0944 (5)	0.1272 (4)	3.9 (2)
O(7)	0.3278 (5)	-0.0715 (4)	0.2053 (3)	4.7 (1)
C(8)	0.4929 (9)	-0.1579 (6)	0.1938 (5)	5.6 (2)
C(9)	0.431 (1)	-0.3038 (6)	0.2082 (5)	6.3 (2)
C(10)	0.2605 (9)	-0.3382 (5)	0.1374 (4)	4.5 (2)
C(11)	0.0986 (8)	-0.2369 (5)	0.1356 (4)	4.6 (2)
O(12)	0.2495 (7)	-0.4420 (4)	0.0885 (3)	7.3 (2)

Fig. 1. *ORTEP* drawing of the molecular structure with the crystallographic numbering scheme. The ellipsoids correspond to 30% probability contours of atomic displacement.

Discussion. The numbering scheme and the overall conformation of the compound studied is shown in Fig. 1. Table 2 lists the bond distances and angles.

The Cremer & Pople (1975) ring-puckering parameters $Q = 0.515$ (6) Å, $\theta = 169.7$ (6) and $\varphi = 173$ (4)° calculated for the pyranoid ring indicated the $^6C_9$ chair conformation with a small distortion towards the ^{10}E half chair. The main reason for this distortion is the presence of the sp^2-hybridized C atom rather than the dioxolane ring. This conclusion agrees well with the results of a molecular-mechanics calculation, using the MM2(85) program (Allinger, 1987), performed for the title compound and for tetrahydro-2-methoxy-2-methyl-4H-pyran-4-one as a model compound without the dioxolane ring but with the anomeric and exo-anomeric effects. In both cases the optimized geometry of the pyranoid ring is almost the same but closer to the ideal chair geometry than in the crystal under investigation. The calculated θ parameters for both compounds were 177 and 176°, respectively.

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

O(1)—C(2)	1·444 (7)	C(6)—C(11)	1·529 (7)
O(1)—C(6)	1·427 (6)	O(7)—C(8)	1·426 (7)
C(2)—C(3)	1·502 (9)	C(8)—C(9)	1·528 (8)
C(3)—O(4)	1·443 (8)	C(9)—C(10)	1·496 (9)
O(4)—C(5)	1·437 (7)	C(10)—C(11)	1·498 (8)
C(5)—C(6)	1·519 (8)	C(10)—O(12)	1·203 (6)
C(6)—O(7)	1·417 (6)		

C(2)—O(1)—C(6)	112·2 (4)	C(5)—C(6)—C(11)	111·2 (5)
O(1)—C(2)—C(3)	109·9 (5)	O(7)—C(6)—C(11)	111·2 (4)
C(2)—C(3)—O(4)	111·1 (5)	C(6)—O(7)—C(8)	113·6 (4)
C(3)—O(4)—C(5)	108·8 (4)	O(7)—C(8)—C(9)	110·5 (5)
O(4)—C(5)—C(6)	112·3 (5)	C(8)—C(9)—C(10)	111·4 (5)
O(1)—C(6)—C(5)	110·7 (4)	C(9)—C(10)—C(11)	115·3 (4)
O(1)—C(6)—O(7)	110·9 (4)	C(9)—C(10)—O(12)	122·7 (5)
O(1)—C(6)—C(11)	105·7 (4)	C(11)—C(10)—O(12)	122·0 (5)
C(5)—C(6)—O(7)	107·3 (4)	C(6)—C(11)—C(10)	111·5 (5)

The dioxolane ring with $Q = 0.554$ (6) Å, $\theta = 176.1$ (6) and $\varphi = 49$ (8)° has the $^6C_3$ chair conformation. The conformation of the whole molecule with the axial positions of the O(1) and O(7) atoms with regard to the pyranoid and dioxolane rings, respectively, as well as the mutual orientation of both chair rings [the dihedral angles C(2)—O(1)—C(6)—O(7) and O(1)—C(6)—O(7)—C(8) are -65.5 (5) and -56.5 (5)°, respectively] is a result of the presence of the anomeric and *exo*-anomeric effects (Kirby, 1983).

The carbonyl oxygen has the pseudoequatorial orientation with an O(12)—C(10)—C(11)—C(6)

torsion angle of -139.3 (5)°. There are no significant intermolecular steric interactions.

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Structure of Pyridazine at 100 K

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Abstract. $C_4H_4N_2$, $M_r = 80.09$, monoclinic, $P2_1/n$, $a = 3.7870$ (6), $b = 10.7415$ (29), $c = 9.721$ (6) Å, $\beta = 91.401$ (27)°, $V = 395.32$ Å^3, $Z = 4$, $D_x = 1.346$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.083$ mm^{-1}, $F(000) = 168$, $T = 100$ K, $R = 0.0495$ for 1732 unique observed reflections. The observed valence angles agree very closely with those measured for free pyridazine studied by combined analysis of electron diffraction, microwave and liquid-crystal NMR data, but there are significant differences in bond lengths, which can probably be attributed to crystal packing effects.

Introduction. We have recently developed the technique whereby gas-phase structural data (electron diffraction and rotational constants) can be combined with dipolar couplings obtained for solutions in liquid-crystal solvents (Cradock, Liescheski, Rankin & Robertson, 1988; Liescheski & Rankin, 1989). In most cases the resulting structures depend on no geometrical assumptions other than the molecular symmetry, and all the parameters can be refined: nevertheless, the precision far exceeds that obtainable by either electron diffraction, rotational spectroscopy or NMR spectroscopy alone. Indeed,