Preliminary communication

Conformation in the crystalline state of tri-*O*-acetyl-β-D-arabinopyranosyl bromide*

P. W. R. CORFIELD, J. D. MOKREN, P. L. DURETTE‡, and D. HORTON
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210 (U. S. A.)

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The conformations of a number of crystalline, pyranoid sugars and derivatives have been determined by X-ray crystallography[1], but to date there have been no reports in the literature recording such determinations for simple acetylated sugars or acylated aldopyranosyl halides. The conformational behavior of the latter class of compounds in solution is noteworthy in view of their propensity to adopt chairlike conformations having the halogen atom axial, even at the expense of forcing most[2], or even all[2,3], of the ring substituents into axial orientation. It was of interest to determine the solid-state conformations of certain acylated aldopyranosyl halides to (*a*) ascertain whether there is agreement between the solid-state conformation and the favored conformation in solution, (*b*) determine the extent of distortion from the ideal-chair geometry caused by multiple axial substitution, (*c*) correlate dihedral angles between geminal and vicinal protons, determined for the crystal, with proton–proton coupling-constants determined by n.m.r. spectroscopy, and (*d*) determine the favored orientations of the acyloxy groups in the solid state.

As part of a detailed study[4] of the conformations of acylated aldopentopyranose derivatives in solution, it has been shown[2] by n.m.r. spectroscopy that tri-*O*-acetyl-β-D-arabinopyranosyl bromide (**1**) and the corresponding chloride (**2**) in solution in chloroform-*d* strongly favor the *1C*(D) conformation having the substituents at C-1 and C-4 axial and those at C-2 and C-3 equatorial. The present studies by X-ray crystallography show that **1** and **2** adopt the *1C*(D) conformation in the solid state also. Crystals of **1** are orthorhombic; space group $P2_12_12_1$, having $a = 7.64(1)$, $b = 8.77(1)$, and $c = 20.88(3)$ Å. There are four molecules in the unit cell. The intensities of 1087 independent reflections were obtained by

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‡Present address: Institut für Organische Chemie und Biochemie, Universität Hamburg, 2 Hamburg 13, Bundesrepublik Deutschland.

counter methods with $\theta - 2\theta$ scans to $\sin\theta/\lambda = 0.565$. A graphite monochromator was used to select MoKα radiation, and 789 reflections were recorded above background $[F^2 - 2\sigma(F^2)]$.

The bromine and the 18 other non-hydrogen atoms were found by the usual heavy-atom methods. The hydrogen atoms were readily located on a difference Fourier map. The structure was refined by least-squares, with a block-diagonal approximation. Convergence was reached with a conventional R factor of 0.045. Anisotropic thermal parameters were allowed for all of the heavier atoms, and the anomalous contribution from the bromine atom was included. Positional and isotropic thermal parameters for the ring-hydrogen atoms were allowed to vary, but the methyl hydrogen parameters were fixed.

In the crystalline state, molecules of **1** exist in the *1C*(D) conformation as shown, with the bromine atom on C-1 and the acetoxyl group on C-4 in axial orientation and tilted slightly outward from the "ideal" axial disposition. The dihedral angles within the ring show that the chair in this substituted sugar is flattened relative to that in an unsubstituted aldopyranose[5,6] (see Table I), the average dihedral angle being 54.2°, as compared to an average angle of 57.7° in β-DL-arabinopyranose. The shape of the ring in **1** is comparable with that in cyclohexane[7], where the dihedral angle of the ring is 55.9°.

TABLE I

DIHEDRAL ANGLES IN TRI-*O*-ACETYL-β-D-ARABINOPYRANOSYL BROMIDE (1)

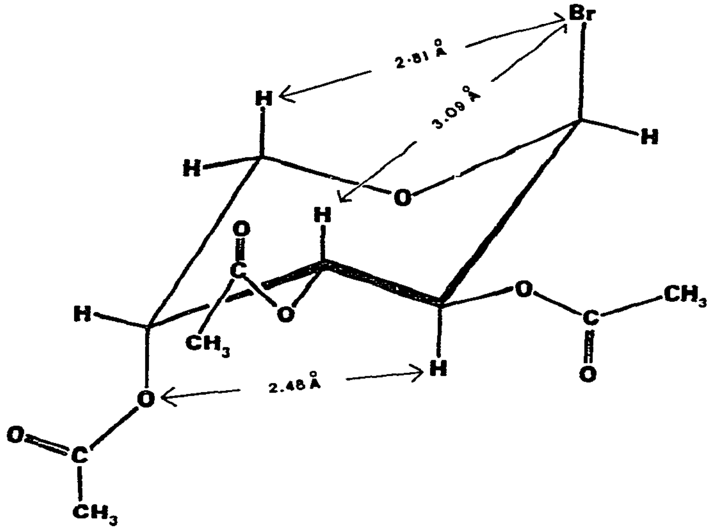
Proton–proton dihedral angles in the crystal	*(degrees)*	*Proton–proton spin-couplings in chloroform-*d *solution*[2] *(Hz)*		*Dihedral angles*[a] *describing the shape of the ring*		
				Angle	*Compound* **1** *(degrees)*	β-DL-*Arabinopyranose*[6] *(degrees)*
H-1–H-2	64 ±7	$J_{1,2}$	3.8	O-5–C-3	56	58
H-2–H-3	176 ±5	$J_{2,3}$	11.5	C-1–C-4	54	57
H-3–H-4	41 ±4	$J_{3,4}$	3.4	C-2–C-5	53	55
H-4–H-5*e*	86 ±5	$J_{4,5e}$	1.8 [b]	C-3–O-5	53	56
H-4–H-5*a*	44 ±5	$J_{4,5a}$	0.7 [b]	C-4–C-1	55	60
H-5*e*–H-5*a* [c]	117 ±5	$J_{5e,5a}$	−13.3	C-5–C-2	55	60

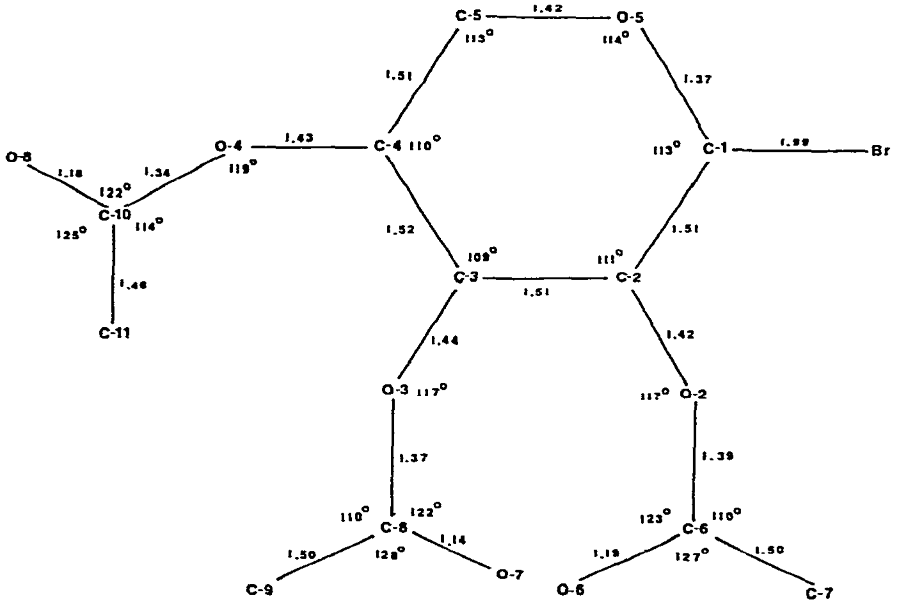
[a] ±1°. [b] The H-5 signal resonating at higher field is assigned as H-5*e*. [c] Geminal angle.

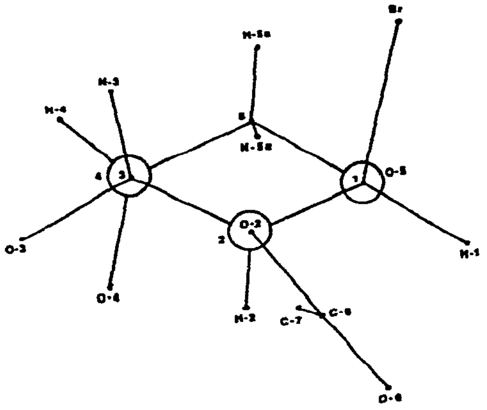
The positions of the ring-hydrogen atoms are not known very precisely, as the scattering power of these atoms is much less than that of the bromine atom, but the proton–proton dihedral angles observed show broad correlation with those estimated from n.m.r. spin-coupling values for **1** in solution (see Table I). However, definite quantitative discrepancies exist between the dihedral angles observed and those estimated from spin-couplings by equations of the Karplus type, even allowing for electronegativity factors[1,8,9]; these observations serve to reiterate the need for caution[1] in attempts to assign precise angular dependencies from spin-coupling data.

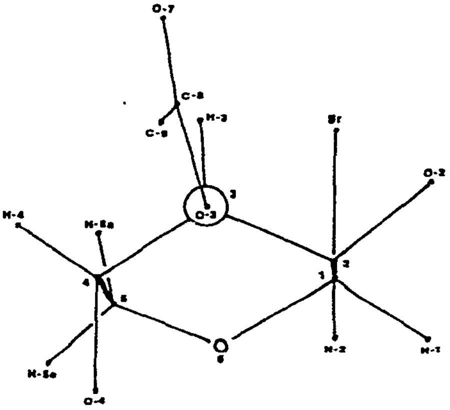
The bond lengths within the pyranoid ring of **1** differ little from those observed[6] for β-DL-arabinopyranose. The C-1–O-5 bond in **1** is significantly shorter than the C-5–O-5 bond, and the C-5–O-5–C-1 angle is significantly greater than tetrahedral.

The acetoxyl groups on C-3 and C-4 are distorted only slightly from the completely extended conformation, having the methine and methyl carbon atoms antiparallel, found for other ester groups in the solid state[10]. In the structure of **1** are observed two types of rotation away from a planar conformation in which the carbonyl group would eclipse the methine C–H bond. The *first* type is a rotation about the ring-






Br
H-5a
H-3
H-4
5
H-5e
4
3
1
O-5
O-3
O-2
2
H-1
O-4
H-2
C-7
C-6
O-6


O-7
C-8
H-3
C-9
Br
O-2
3
O-3
H-4
H-5a
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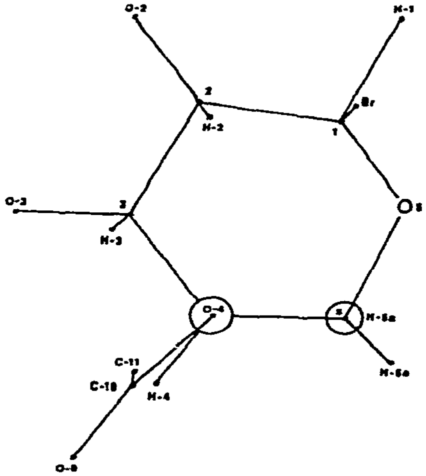
1
4
5
O
5
H-2
H-1
H-5e
O-4


O-2
H-1
2
Br
H-2
1
O-3
3
O5
H-3
O-4
5
H-5a
C-11
C-10
H-4
H-5e
O-8

carbon–oxygen bond; the corresponding dihedral angles for the groups at C-2, C-3, and C-4 in **1** are 43°, 10°, and 11°, respectively. The extensive distortion at C-2 is analogous to similar findings for methyl 2,3,5-tetra-*O*-acetyl-β-D-galactofuranuronate[11]; a similar deviation appears probable in an acetylated heptitol[12]. The *second* type of rotation in the acetoxyl groups is about the O–COCH$_3$ bond, away from the antiparallel disposition[10]. These two rotations are very slight in **1**, being 3°, 10°, and 7° for the C-2, C-3, and C-4 acetoxyl groups, so that the carbon atoms of the acetoxyl groups are almost coplanar with the corresponding ring-carbon atoms.

Preliminary X-ray crystallographic data for the chloride **2** indicate broad similarities to the conformational structure reported here for **1**.

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