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Synthesis of 3,4-di-*O*-acetyl-2,5-anhydro-1,6-dideoxy-1,6-diiodo-D-mannitol. Comparison of NMR spectral results for the solid state and solution with those of the X-ray structural determination

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Abstract

3,4-Di-*O*-acetyl-2,5-anhydro-1,6-dideoxy-1,6-diiodo-D-mannitol (**3**) is prepared from 2,5-anhydro-D-mannitol (**1**) in three steps. The solution and solid-state NMR spectra of **3** indicate considerable variation in conformation. In solution, it adopts, on average, a symmetric $^4T_3$ conformation, whereas in the solid state it adopts an asymmetric conformation as revealed by ^{13}C NMR cross polarization and magic angle spinning techniques. A single-crystal X-ray structure analysis confirmed the asymmetric conformation of **3** in a monoclinic crystal, space group $P2_1$ with $a = 8.9608(4)$, $b = 8.6348(5)$, $c = 9.6468(4)$ Å, $\beta = 96.139(4)°$, $V = 742.1(1)$ Å^3, $D_c = 2.085$ g cm^{-3}, μ (MoK_α) = 4.2 mm^{-1}, and $Z = 2$. The structure was refined to $R = 0.039$ and $R_w = 0.047$ for 5181 observed reflections. The furanoid ring of **3** adopts an envelope E_5 conformation slightly distorted towards $^4T_5$, with puckering parameters $\varphi = 313.49°$ and $q = 0.37$ Å. The asymmetric conformation is rationalized in terms of the weak packing forces in the crystal.

Keywords: X-ray structure; CPMAS NMR spectroscopy; NMR spectroscopy; Anhydro sugar

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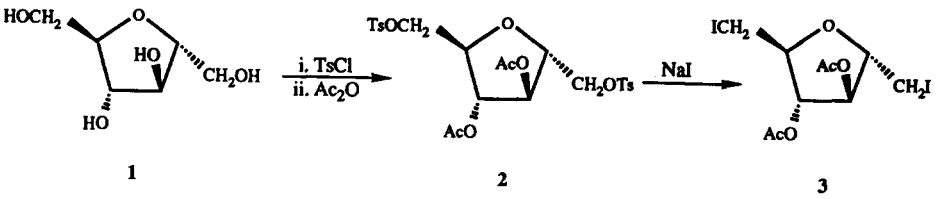
1. Introduction

The present study concerns a compound in which the conformation in solution is not that which exists in the solid state. It shows the advantage of solid-state NMR spectroscopy, as an analytical tool complementary to X-ray crystallography, over solution NMR spectroscopy for studying conformational analysis since only one conformer is present in the solid state [1–5]. Thus, spectral complexities due to solvent and temperature effects on conformational equilibria are eliminated. In an earlier work on the conformation of 2,5-anhydro-D-mannitol (**1**) [6,7], the parent of the title compound, it was shown that the compound undergoes rapid ring twisting motions in solution [8]. Its ^{13}C NMR spectrum showed only half as many peaks as there are carbon atoms due to the symmetry of the averaged structure, whereas in the solid state its CPMAS ^{13}C spectrum [9] showed one peak for each carbon atom. The X-ray analysis [10] demonstrated that the molecule lacks the expected C_2 symmetry as its conformation deviates from the ideal $^4T_3$ structure by a pseudorotation angle (P) of $-11.7°$ and pseudorotation amplitude [11] (τ_m) of 39.9°. In a recent study on the conformation of 3,4-di-*O*-acetyl-2,5-anhydro-1,6-di-*O*-(*p*-tolylsulfonyl)-D-mannitol (**2**), the precursor of the title compound, we showed that the compound has C_2 symmetry in the crystalline state [12]. Its furanose ring adopts a perfect twist ^3_4T conformation, with P of 180° and τ_m of 24.41°. From the foregoing studies, it is apparent that the molecular distortion of **1** is caused by the strong intermolecular forces that arise from the different types of hydrogen-bonding interactions in the crystal.

In the present work, we report the synthesis of the title compound, 3,4,-di-*O*-acetyl-2,5-anhydro-1,6-dideoxy-1,6-diiodo-D-mannitol (**3**). The conflict between the structure predicted from solution and solid-state NMR data has led us to determine its conformation and 3D molecular structure by X-ray crystallography. Our main objective of these studies is to provide information on the conformational properties of 2,5-anhydro sugars that might be helpful in formulating a more detailed understanding of their chemical and biological behavior.

2. Experimental

General.—The melting point was determined with a Thomas–Hoover "Unimelt" oil-bath apparatus and is uncorrected. Solvents for reactions were of the highest grades; organic extracts were dried over anhydrous magnesium sulfate. Thin-layer chromatography was carried out using precoated sheets (Merck Silica Gel-60, layer thickness 0.2 mm). ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on a Bruker spectrometer at 200 and 50.3 MHz, respectively. Tetramethylsilane (Me_4Si) was used as the internal standard. Solid-state cross-polarization magic-angle-spinning ^{13}C NMR spectra were obtained at 50.3 MHz (4.7 Tesla) using a Bruker MSL 200 spectrometer. Samples were loaded in a 4-mm ZrO_2 rotor with a Kel-F cap and spun at 6.1 KHz with air. Data acquisition was via a single-contact Hartmann–Hahn cross-polarization pulse sequence [13]. The acquisition parameters were as follows: 5 ms ^1H 90° pulse, 75 ms cross-polarization time, and a 3 s recycle delay. A total of 1500 transients were



1 2 3

Ts = $CH_3C_6H_4SO_2$
Ac = $COCH_3$

Scheme 1.

recorded, and an exponential line broadening factor of 10 Hz was applied. The ^{13}C chemical shift values were recorded on the δ-scale indirectly referenced through adamantane (external reference) to Me_4Si.

3,4-*Di*-O-*acetyl*-2,5-*anhydro*-1,6-*dideoxy*-1,6-*diiodo*-D-*mannitol*.—A solution of 3,4-di-*O*-acetyl-2,5-anhydro-1,6-di-*O*-(*p*-tolylsulfonyl)-D-mannitol [14] (5.6 g, 10 mmol) was refluxed with sodium iodide (6 g, 40 mmol) in anhydrous 2-butanone for 10 h. The mixture was cooled, filtered, and the precipitated salt of sodium *p*-toluene sulfonic acid was washed with anhydrous 2-butanone. The filtrate and washings were combined, concentrated to dryness, and the residue was extracted with CH_2Cl_2 (3×50 mL). The combined extracts were filtered and evaporated to dryness under diminished pressure. The resulting yellow syrup was stirred with 100 ml of water and a few crystals of sodium thiosulfate until the free iodine had been removed. The solid formed was removed by filtration, washed with water, and dried (3.8 g, 82%). It was crystallized from absolute EtOH; mp 54–55°C. ^1H NMR: δ 2.12 (s, $COCH_3$), 3.26 (dd, H-1, $J_{1,2}$ 6.2 Hz, $J_{1,1'}$ 10.56 Hz), 3.32 (dd, H-1', $J_{1',2}$ 6.35 Hz), 4.15 (m, H-2, $J_{2,3}$ 3 Hz), 5.2 (d, H-3, $J_{3,4}$ 1 Hz). ^{13}C NMR: δ 4.67 (C-1), 20.73 (CH_3), 80.24 (C-3), 82.40, (C-2), 169.58 (C = 0). Anal. Calcd for $C_{10}H_{12}I_2O_5$: C, 25.76; H, 2.60; I, 54.48. Found: C, 25.74; H, 3.00; I, 54.64.

X-ray crystal structure determination.—Intensity data were collected on an Enraf–Nonius CAD4 diffractometer equipped with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at 23°C. Unit-cell parameters were obtained from setting angles of 25 reflections having $26 < 2\theta < 30°$. The parameters utilized in intensity data collection and refinement are summarized in Table 1 together with the crystal data. A quadrant of data was collected to $\theta_{max} = 35°$, and a second quadrant to $\theta_{max} = 30°$. Intensity standards decreased by 6.3% in intensity, and a linear correction was applied. Absorption corrections were based on ψ scans, with minimum relative transmission coefficient 83.2%.

The structure was solved by heavy-atom methods and refined by full-matrix least squares based upon F with weights $w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$ using the MolEN programs [15]. Nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference maps but were not refined. Atomic coordinates and

Table 1
Data collection and crystallographic parameters for 3,4-di-*O*-acetyl-2,5-anhydro-1,6-dideoxy-1,6-diiodo-D-mannitol (**3**)

Molecular formula	$C_{10}H_{12}I_2O_5$
Molecular weight	466.0
Melting point (°C)	54–55
Crystal dimensions (mm)	$0.35\times0.40\times0.52$
Crystal system	monoclinic
Space group	$P2_1$
Cell dimensions (Å)	
a	8.9608(4)
b	8.6348(5)
c	9.6468(4)
β(°)	96.139(4)
Volume (Å^3)	742.1(1)
Calculated density (g cm^{-3})	2.085
Z (molecules/cell)	2
F (000)	436
μ (mm^{-1})	4.20
Radiation (graphite monochromator)	Mo$K\alpha$
Data collection	CAD4
Collection method	ω–2θ
2θ range (°)	2–70
Scan rate (deg. min^{-1})	0.66–3.30
No. of data collected	6836
Unique reflections	6516
$I > 3\sigma(I)$	5181
S (154 variables)	2.464
Maximium shift	0.01σ
Max/min residual density (eÅ^{-3})	1.53/−0.40
Extinction coefficient	$2.46(4)\times10^{-6}$
Final residual factors	
R	0.039
R_w	0.047

equivalent isotropic thermal parameters, along with their esd's, are given in Table 2 [1]. All calculations were performed on a VAX 3600 computer. Atomic scattering factors were obtained from the *International Tables for X-ray Crystallography* [16]. Enantiomer refinement under identical circumstances gave $R = 0.044$, $R_w = 0.054$, and $S = 2.822$.

3. Results and discussion

The title compound **3** was prepared by treatment of 2,5-anhydro-D-mannitol (**1**) with 2 molar equivalents of *p*-toluenesulfonyl chloride, followed by acetylation of the

[1] Lists of observed and calculated structure-amplitudes, anisotropic thermal parameters, hydrogen coordinates and isotropic thermal parameters, and torsion angles for **3** have been deposited with the Cambridge Crystallographic Data Centre and may be obtained on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Table 2
Atomic coordinates and equivalent isotropic thermal parameters for 3,4-di-*O*-acetyl-2,5-anhydro-1,6-dideoxy-1,6-diiodo-D-mannitol (**3**).

Atom	*x*	*y*	*z*	B_{eq} (Å^2) [a]
I-1	0.40565(3)	0	0.51724(3)	6.047(6)
I-2	0.59432(2)	0.15307(5)	−0.09990(3)	4.887(5)
O-2	0.5991(3)	0.0844(3)	0.2470(3)	3.92(5)
O-3	0.8597(3)	−0.2066(3)	0.2726(3)	4.39(5)
O-4	0.9835(2)	0.1407(3)	0.2018(3)	3.78(4)
O-5	1.0317(5)	−0.2364(5)	0.4511(5)	9.4(1)
O-6	1.0684(4)	−0.0363(6)	0.0639(5)	8.67(9)
C-1	0.6396(5)	−0.0061(6)	0.4859(4)	4.40(7)
C-2	0.6602(4)	−0.0379(4)	0.3357(3)	3.31(5)
C-3	0.8279(4)	−0.0508(4)	0.3125(4)	3.23(5)
C-4	0.8435(3)	0.0611(4)	0.1933(3)	2.99(5)
C-5	0.7190(3)	0.1773(4)	0.2099(3)	3.17(5)
C-6	0.6703(4)	0.2772(4)	0.0862(4)	3.99(7)
C-7	0.9639(5)	−0.2876(5)	0.3480(4)	4.13(7)
C-8	0.9826(6)	−0.4442(5)	0.2871(6)	5.2(1)
C-9	1.0882(4)	0.0814(6)	0.1279(5)	4.77(8)
C-10	1.2233(5)	0.187(1)	0.1325(7)	7.3(2)

[a] $B_{eq} = (8\pi^2/3)\Sigma_i \Sigma_j U_{ij} a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$

resultant 1,6-di-*O*-*p*-toluenesulfonate with acetic anhydride in pyridine to afford the completely blocked 3,4-di-*O*-acetyl-2,5-anhydro-1,6-di-*O*-(*p*-tolylsulfonyl)-D-mannitol (**2**). Subsequent treatment of the latter with four molar equivalents of sodium iodide in boiling 2-butanone afforded **3** in 82% yield as a crystalline material. The solution and solid-state ^{13}C NMR spectra of **3** are shown in Fig. 1, together with the carbon atom assignments.

The ^{13}C NMR solution spectrum is consistent with a structure having two-fold symmetry. It disclosed signals for only three carbon atoms of the sugar residue at δ 20.73, 80.24 and 82.4 ppm and two for the acetyl CH_3 and C = O groups at δ 4.67 and 169.58 ppm, respectively. It indicated that a structure averaging readily occurred in solution, and thus averaging the resonances for the carbon atoms at the corresponding positions. The ^1H NMR data supported the assigned structure; it showed a high degree of symmetry, and the coupling constants indicated $^4T_3$ as the average conformation in solution. The solid-state NMR spectrum, however, clearly showed a doubling of all signals in the ratio of 1 : 1. There are two resonances observed for the carbonyl sites at 169 and 169.5 ppm and a total of four resonances for the furanose ring carbons. The two methyl sites resonate at 20 ppm and the broad resonance of the ICH_2-sites resonate at 12 ppm. The line broadening of the latter can be attributed to the $^{13}C-^{127}I$ dipolar coupling [17–19]. Such broadened or split ^{13}C and ^{31}P resonances have been observed for sites bound to quadrupolar nuclei, where the magnitude of the line broadening is a function of the quadrupole coupling constant [20]. From the solid-state NMR spectrum, it became apparent that a single asymmetric conformation of **3** was indeed present. Such a conformation creates a unique environment for the nominally equivalent carbon atoms,

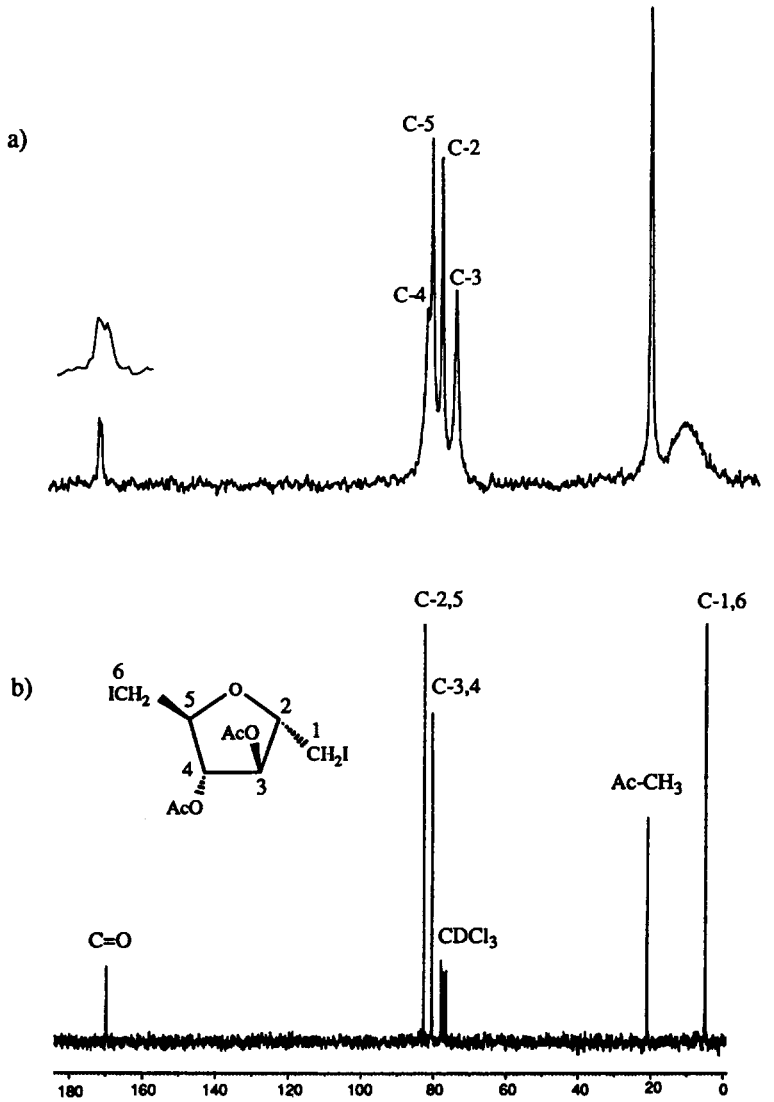


Fig. 1. The solid-state ^{13}C NMR spectrum of 3,4-di-*O*-acetyl-2,5-anhydro-1,6-dideoxy-1,6-diiodo-D-mannitol (**3**) is shown in trace a. There is no evidence of a spinning sideband pattern from the carbonyl resonance; sidebands are suppressed because of the moderate spin rate, 6.1 kHz, and the low field, 3.7 T. The solution-state ^{13}C NMR spectrum is shown in trace b.

and hence one sees one peak for each carbon atom. This would not be expected if the molecule possessed a plane of symmetry orthogonal to the ring plane through O-2 and the midpoint of the C-3–C-4 bond.

The crystal structure of **3** has been determined in order to confirm the asymmetric conformation and to clarify the conformational properties of the molecule. It is repre-

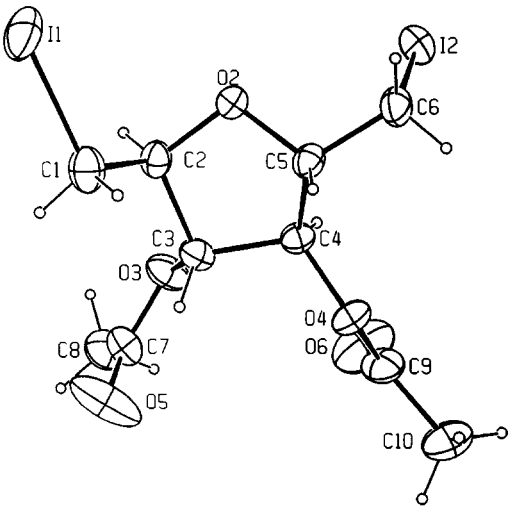


Fig. 2. Molecular structure and atomic numbering of 3,4-di-*O*-acetyl-2,5-anhydro-1,6-dideoxy-1,6-diiodo-D-mannitol **2**. Nonhydrogen atoms are represented with 40% ellipsoids and hydrogen atoms with circles of arbitrary radius.

sented as an ORTEP drawing [21] (Fig. 2), which also shows the atom numbering in the molecule. The bond lengths, bond angles, and selected torsion angles with their estimated standard deviations are listed in Table 3.

Careful examination of the molecular structure reveals that the molecule is far from symmetric. Furanose ring bond lengths O-2–C-5 [1.417(4) Å] versus O-2–C-2 bond [1.431(4) Å] and C-5–C-4 [1.522(4)] versus C-2–C-3 bond [1.547(5) Å] differ by marginally significant amounts. Conclusive evidence of the asymmetrical nature of **3** can be drawn from the orientation of the halogen atoms as well as the acetoxy groups about the ring. The orientation of I-1 about the C-1–C-2 bond is *gauche–trans* to O-2 and C-3, with the torsion angles I-1–C-1–C-2–O-2 and I-1–C-1–C-2–C-3 being 63.9(4)° and −177.2(2)°, respectively, whereas the orientation of I-2 about the C-5–C-6 bond is *gauche–gauche* to O-2 and C-4, with the torsion angles I-2–C-6–C-5–O-2 and I-2–C-6–C-5–C-4 being −63.9(4)° and 57.4(4)°, respectively.

The orientation of the acetate groups is similar to that observed in many other peracetylated pyranose molecules, with the C = O groups syndiaxial to the C–H bond at the ring carbon atom to which the group is attached [22–26]. The acetoxy group on C-2 is so oriented that the C = O bond almost eclipses the exocyclic C–H bond, with C-7–O-3–C-3–C-2 = −122.1(4)° whereas the acetoxy group on C-4 is midway between the eclipsed and staggered orientations with respect to the exocyclic C–H bond, with C-9–O-4–C-4–C-5 = −149.1(3)°.

The furanoid ring of **3** adopts an envelope E_5 conformation slightly distorted towards $^4T_5$, with a phase angle (P) of 46.92° and a pseudorotation amplitude (τ_m) of 39.56°. The corresponding puckering parameters [27] are $\varphi = 313.49°$ and $q = 0.37$ Å. Displacement of the atoms from the least-squares plane suggests the E_5 conformation. Four

Table 3
Bond lengths, bond angles and selected torsion angles in 3,4-di-*O*-acetyl-2,5-anhydro-1,6-dideoxy-1,6-diiodo-D-mannitol (**3**)

Atoms	Length (Å)	Atoms	Length (Å)	Atoms	Length (Å)
I-1–C-1	2.150(4)	O-4–C4	1.425(4)	C-3–C-4	1.519(5)
I-2–C-6	2.139(4)	O-4–C-9	1.339(5)	C-4–C-5	1.522(4)
O-2–C-2	1.431(4)	O-5–C7	1.193(6)	C-5–C-6	1.499(5)
O-2–C-5	1.417(4)	O-6–C-9	1.193(7)	C-7–C-8	1.491(6)
O-3–C-3	1.437(4)	C-1–C-2	1.506(5)	C-9–C-10	1.510(8)
O-3–C-7	1.321(5)	C-2–C-3	1.547(5)		
Atoms	Angle (°)	Atoms	Angle (°)	Atoms	Angle (°)
C-2–O-2–C-5	108.5(2)	O-3–C-3–C-2	109.2(3)	O-2–C-5–C-6	111.3(3)
C-3–O-3–C-7	119.8(3)	O-3–C-3–C-4	110.9(3)	C-4–C-5–C-6	116.8(3)
C-4–O-4–C-9	116.6(3)	C-2–C-3–C-4	103.5(2)	I-2–C-6–C-5	114.8(2)
I-1–C-1–C-2	111.2(2)	O-4–C-4–C-3	114.5(2)	O-3–C-7–O-5	122.0(4)
O-2–C-2–C-1	111.3(3)	O-4–C-4–C-5	109.1(3)	O-3–C-7–C-8	111.4(4)
O-2–C-2–C-3	106.4(3)	C-3–C-4–C-5	102.2(3)	O-5–C-7–C-8	126.5(4)
C-1–C-2–C-3	111.9(3)	O-2–C-5–C-4	103.7(3)	O-4–C-9–O-6	121.8(4)
O-4–C-9–C-10	111.1(5)	O-6–C-9–C-10	127.0(5)		
Atoms	Angle (°)	Atoms	Angle (°)	Atoms	Angle (°)
C-5–O-2–C-2–C-3	−19.1(3)	C-3–C-4–C-5–O-2	−39.3(3)	C-9–O-4–C-4–C-3	97.1(4)
C-2–O-2–C-5–C-4	36.9(3)	C-7–O-3–C-3–C-2	−122.1(4)	C-9–O-4–C-4–C-5	−149.1(3)
O-2–C-2–C-3–C-4	−6.3(3)	C-7–O-3–C-3–C-4	124.5(4)	O-4–C-4–C-5–O-2	−160.9(3)
C-2–C-3–C-4–C-5	27.0(3)				

atoms, O-2, C-2, C-3, and C-4 are nearly coplanar with average deviation 0.03 Å. The fifth atom, C-5, is displaced by 0.56 Å in the *exo* direction with respect of this plane.

In the present work, it was interesting to observe that compound **3** shares similar structural features as those of its parent compound 2,5-anhydro-D-mannitol (**1**). Both

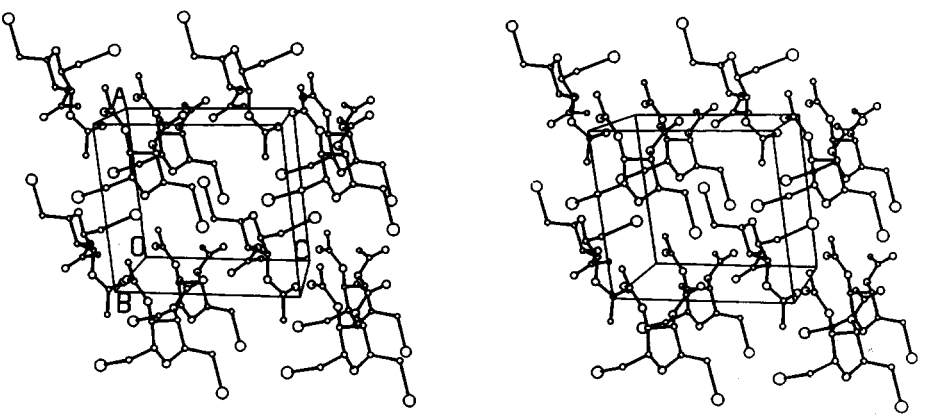


Fig. 3. Stereoscopic representation of the crystal packing for 3,4-di-*O*-acetyl-2,5-anhydro-1,6-dideoxy-1,6-diiodo-D-mannitol (**3**).

compounds adopt asymmetric envelope conformations in the crystalline state. The bond lengths and bond angles of their furanose rings are almost equal and within the limits of experimental errors, except for the bond length C-2–O-2 [1.417(4) Å] in **3**, which is significantly shorter by 6σ than its corresponding bond length [1.450(4) Å] in **1**. This difference may be attributed to the change in the nature and distribution in the substituents around the ring. The molecular distortion of **3** in the crystal, unlike **1**, however, can be attributed to weak crystal-packing forces, since hydrogen-bonding substituents are not present. The crystal packing is illustrated in Fig. 3.

Acknowledgements

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