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# Crystal and Molecular Structure of 1-Methyl-6-O-*p*-toluenesulfonyl-alpha-D-glucopyranoside Dihydrate

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Grown from aqueous solution, 1-methyl-6-O-*p*-toluenesulfonyl-alpha-D-glucopyranoside dihydrate is monoclinic, space group $P2_1$, $a = 6.6236(4)$, $b = 6.4708(4)$, $c = 20.1758(11)$ Å; $\beta = 92.836(2)°$; $Z = 2$; $V = 863.68(9)$ Å$^3$. The molecules are interconnected in the solid state by O—H ··· O hydrogen bonds involving bridging water molecules.

**Keywords:** Crystal structure, glucopyranoside, electrophilic carbohydrate

## 1 Introduction

The primary and secondary hydroxyl groups of carbohydrates have comparable reactivity. Hence, synthetic transformations that are selective in their position of reaction take on a particular significance. (1) The reaction of methylglucopyranoside with *p*-toluenesulfonyl chloride in pyridine leads to the selective tosylation of the primary hydroxyl group. (2) The product of this reaction is the *p*-toluenesulfonate of methylglucopyranoside (**1**). It was initially reported (2) as having hydrated and anhydrous forms.

We prepared **1** as an electrophilic sugar reagent (3) to react it with 2-ethynylpyridine for the preparation of a pyridine substituted polyacetylene related to such polymeric materials initially characterized by Blumstein and collaborators (4).

## 2 Experimental

### 2.1 Synthesis

### 2.1.1. *Materials*

Pyridine, *p*-toluenesulfonyl chloride, and $\alpha$-D-methylglucopyranoside were obtained from Aldrich. Pyridine was freshly distilled from calcium hydride before use.

### 2.1.2. *Preparation of 1*

This procedure generally follows that given in (2). A solution of $\alpha$-D-methylglucopyranoside (4.00 g, 21 mmol) in pyridine (36 ml) was added to a solution of *p*-toluenesulfonyl chloride (4.21 g, 22 mmol) in pyridine (10 ml). The mixture was allowed to stand at room temperature for two days. The pyridine was evaporated under reduced pressure at temperatures less than 40°C. The residue was dissolved in chloroform (50 ml) and washed with $KHSO_4$ solution followed by $KHCO_3$ solution. The chloroform solution was dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residual syrup was dissolved in benzene (50 ml) by heating; this solution cooled to a yellow gel-like paste that was filtered and dried in a desiccator. It was dissolved in water (5 ml) and cooled in an ice bath to give 1.3 g (3.7 mmol, 18% yield), m.p. 56–58°; lit. (2) m.p. 56–58° (hydrate).

### 2.1.3. *Crystals of 1*

**1**(37.5 mg) and 2-ethynylpyridine were fused at 75° for one hour. Water (5 ml) was added to this mixture and stirred at 75° for 15 min. The mixture was vacuum filtered and the solution evaporated to leave a magenta film that was vacuum dried. The film was dissolved in water (2 ml) with warming. The solution was allowed to evaporate, and magenta crystals were obtained. These were found to be **1**, colored magenta by traces of polymer.

### 2.2 X-Ray Structure Determination

A single crystal of **1** was selected and mounted on a MiTeGen loop using Paratone oil. The crystal was placed on

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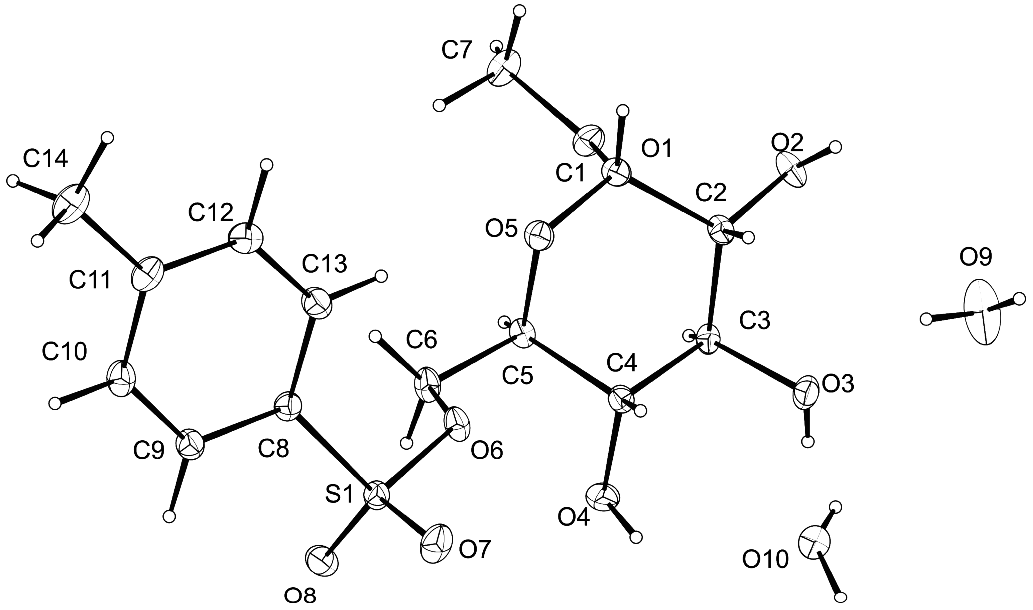

**Fig. 1.** Molecular Structure of the dihydrate of **1**, showing labeling scheme and 50% probability ellipsoids for atoms refined by using anisotropic displacement parameters.

a Bruker-Nonius Kappa Apex2 diffractometer, equipped with graphite-monochromated MoK$\alpha$ radiation, and optically centered. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software (5). Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120 K, using a frame time of 20 sec and a detector distance of 60 mm.

The optimized strategy used for data collection consisted of three phi and eight omega scan sets, with 0.5° steps in phi or omega; completeness was 99.9%. A total of 2570 frames were collected. Final cell constants were obtained

**Table 1.** Crystallographic data for **1**

| *Compound* | *1-Methyl-6-O-p-toluenesulfonyl-alpha-D-glucopyranoside dihydrate (**1**)* |
|---|---|
| Chemical Formula | $C_{14}H_{24}O_{10}S$ |
| $a$, Å | 6.6236 (4) |
| $b$, Å | 6.4708 (4) |
| $c$, Å | 20.1758 (11) |
| $\beta$,° | 92.83 6(2) |
| $V$, Å$^3$ | 863.68 (9) |
| $Z$, $Z$ = | 2, 1 |
| Formula Wt. g/mol | 384.40 |
| Space Group | $P2_1$ |
| $T$, K | 120 (1) |
| $\lambda$ , Å | 0.71073 |
| $\rho_{\mathrm{calc}}$, g cm$^{-3}$ | 1.478 |
| $\mu$, mm$^{-1}$ | 0.239 |
| $\theta_{\max}$; transmission factors | 30.05°; 0.926–0.971 |
| Flack parameter | 0.00(4) |
| $R^a$ (I > 2$\sigma$ (I), 4759 data) | 0.0243 |
| $R_w^b$ (all 4919 data) | 0.0659 |
| $S^c$ | 1.017 |
| No. parameters | 323 |

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ .
[b] $R_w = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma \mathrm{w}(F_o^2)^2]^{1/2.}$
[c] $S = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{2.}$

**Table 2.** Relevant Bond Lengths (Å) and Angles (E) for **I**

| *S(1) - O(6) 1.5675(8)* | *O(5) - C(1) 1.4186(12)* |
|---|---|
| S(1) - O(7) 1.4315(9) | O(5) - C(5) 1.4348(12) |
| S(1) - O(8) 1.4314(8) | O(6) - C(6) 1.4667(13) |
| S(1) - C(8) 1.7537(10) | C(1) - C(2) 1.5306(14) |
| O(1) - C(1) 1.4046(13) | C(2) - C(3) 1.5238(14) |
| O(1) - C(7) 1.4318(14) | C(3) - C(4) 1.5246(14) |
| O(2) - C(2) 1.4203(12) | C(4) - C(5) 1.5230(14) |
| O(3) - C(3) 1.4313(12) | C(5) - C(6) 1.5061(14) |
| O(4) - C(4) 1.4182(12) | |
| O(6) - S(1) - O(7) 104.59(5) | O(2) - C(2) - C(3) 110.12(8) |
| O(6) - S(1) - O(8) 110.19(5) | C(1) - C(2) - C(3) 111.51(8) |
| O(7) - S(1) - O(8) 118.85(6) | O(3) - C(3) - C(2) 107.81(8) |
| O(6) - S(1) - C(8) 104.32(5) | O(3) - C(3) - C(4) 111.18(9) |
| O(7) - S(1) - C(8) 109.33(5) | C(2) - C(3) - C(4) 110.70(8) |
| O(8) - S(1) - C(8) 108.57(5) | O(4) - C(4) - C(3) 110.72(8) |
| C(1) - O(1) - C(7) 112.20(9) | O(4) - C(4) - C(5) 108.72(8) |
| C(1) - O(5) - C(5) 113.18(7) | C(3) - C(4) - C(5) 107.82(8) |
| S(1) - O(6) - C(6) 117.92(7) | O(5) - C(5) - C(4) 108.98(8) |
| O(1) - C(1) - O(5) 112.81(8) | O(5) - C(5) - C(6) 108.01(8) |
| O(1) - C(1) - C(2) 107.67(8) | C(4) - C(5) - C(6) 114.09(9) |
| O(5) - C(1) - C(2) 111.19(8) | O(6) - C(6) - C(5) 107.87(8) |
| O(2) - C(2) - C(1) 109.03(9) | |

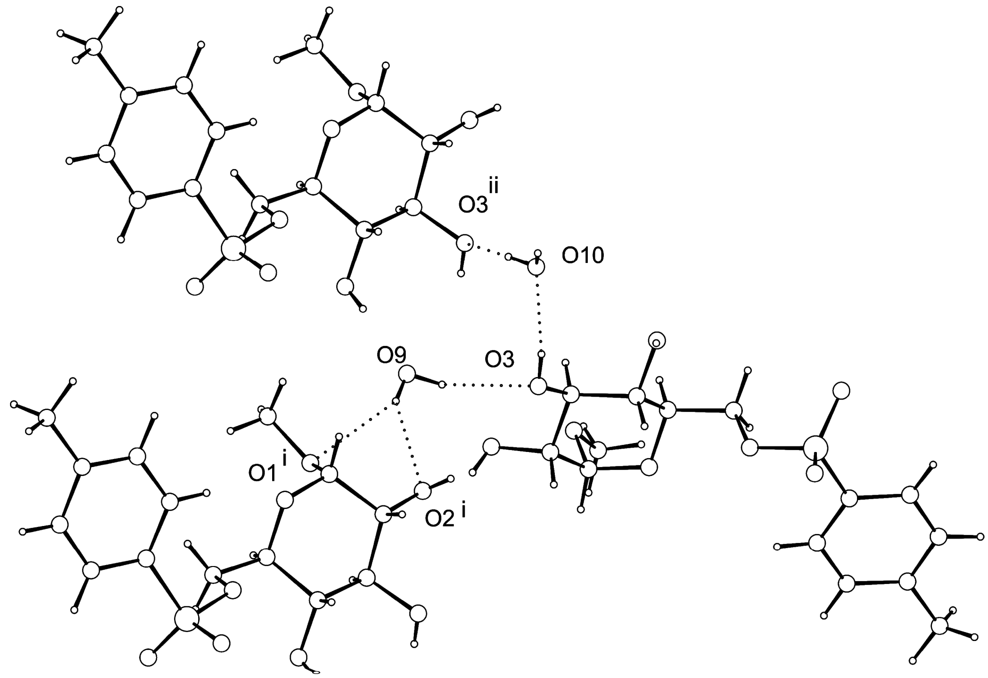

**Fig. 2.** Three molecules of 1, showing the hydrogen bond bridging between the asymmetric unit molecules and symmetry related molecules at (i) $1-x, -\frac{1}{2}+y, -z$ and (ii) $-x, \frac{1}{2}+y, -z$ .

from the xyz centroids of 9885 reflections after integration. From the systematic absences, the observed metric constants and intensity statistics, space group $P2_1$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using SIR-92 (6), and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program (7); drawings were prepared using CAMERON (8). All non-hydrogen atoms were refined using anisotropic displacement parameters; hydrogen atoms were refined using isotropic displacement parameters. Table 1 shows crystallographic data, while Table 2 shows relevant bond lengths and angles.

## 3 Results and Discussion

The molecular structure of **1**, including two molecules of water, is shown in Figure 1. Bond lengths and angles (Table 2) lie within normal ranges, as determined by a Mogul geometry check (9) against similar structural elements in the Cambridge Structural Database (10), as well as by comparison to the structural parameters for methyl $\alpha$-D-glucopyranoside (11). Table 3 contains a list of the O—H $\cdots$ O hydrogen bonds in the structure. Inspection of the Table reveals that hydrate water molecules bridge molecules of **1**, and that there is no direct hydrogen bonding between molecules of **1**. Figure 2 shows a molecule of **1**, with the hydrate molecules bridging to two additional molecules.

## 4 Conclusions

The structure determination establishes that the "hydrate form of **1**" (2) is a dihydrate. Grown from aqueous solution, 1-methyl-6-O-*p*-toluenesulfonyl-alpha-D-glucopyranoside dihydrate is monoclinic, space group

**Table 3.** Hydrogen Bonds in **1**

| *D—H ⋯ A* | *D—H, Å* | *H ⋯ A, Å* | *D ⋯ A, Å* | *D—H ⋯ A,°* | *Symm Opn* |
|---|---|---|---|---|---|
| O2—H2 ⋯ O10 | 0.78(2) | 1.96(2) | 2.7208(12) | 165(2) | $1+x, y, z$ |
| O3—H3 ⋯ O10 | 0.77(3) | 1.99(3) | 2.7381(12) | 165(3) | $x, y, z$ |
| O4—H4 ⋯ O9 | 0.77(2) | 1.98(2) | 2.7468(16) | 172(2) | $-x, -\frac{1}{2}+y, -z$ |
| O9—H92 ⋯ O3 | 0.84(3) | 2.20(3) | 3.0092(14) | 161(3) | $x, y, z$ |
| O9—H93 ⋯ O1 | 0.77(2) | 2.53(2) | 3.2128(15) | 149(2) | $1-x, -\frac{1}{2}+y, -z$ |
| O9—H93 ⋯ O2 | 0.77(2) | 2.37(2) | 3.0356(16) | 145(2) | $1-x, -\frac{1}{2}+y, -z$ |
| O10—H102 ⋯ O3 | 0.82(3) | 2.05(3) | 2.8090(15) | 155(2) | $-x, \frac{1}{2}+y, -z$ |
| O10—H103 ⋯ O2 | 0.80(3) | 1.98(3) | 2.7675(14) | 167(2) | $-x, -\frac{1}{2}+y, -z$ |

$P2_1$, $a = 6.6236(4)$, $b = 6.4708(4)$, $c = 20.1758\,(11)$ Å; $\beta = 92.836(2)^\circ$; $Z = 2$; $V = 863.68(9)$ Å$^3$. The molecules are interconnected in the solid state by O—H $\cdots$ O hydrogen bonds involving bridging water molecules.

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