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The hydrogen-bonding in α-D-galactose. By G. A. JEFFREY and R. SHIONO, *Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania* 15260, *USA*

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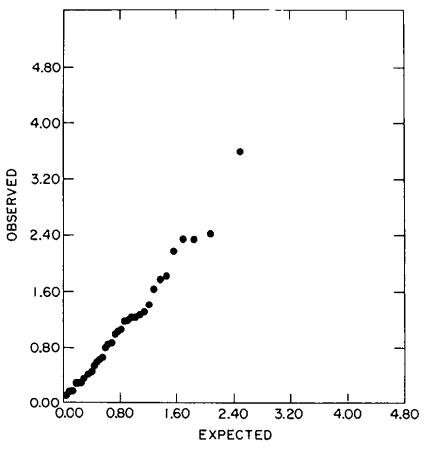
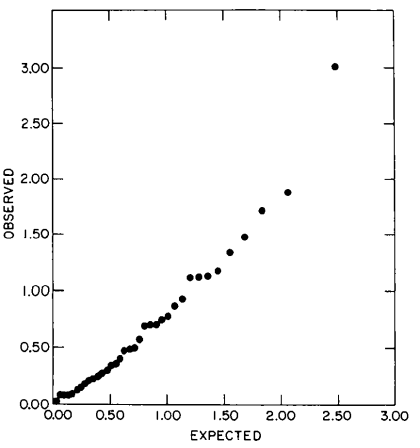
A comparison of two independent crystal structure determinations of α-D-galactose shows close agreement in the positions of the C and O atoms, but significant differences in the interpretation of the hydrogen-bonding. One system of hydrogen bonds agrees better with theoretical predictions than the other.

Two crystal structure determinations of α-D-galactose have been reported recently: (1) Sheldrick (1976) and (2) Ohanessian & Gillier-Pandraud (1976). Both structure determinations were based on diffractometer data, collected with Cu $K\alpha$ radiation, which consisted of 572 and 860 observations respectively. The C and O parameters refined normally by anisotropic full-matrix least squares to residual R values of 0·08 and 0·07. All the H positions were located by difference syntheses and were not refined.



(*a*)

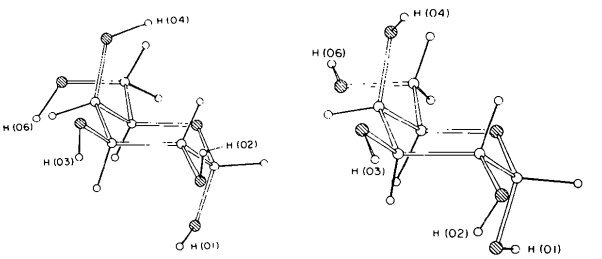


(*b*)

Fig. 1. Half-normal probability plot (Abrahams & Keve, 1971) for the C and O positional parameters in the two structure analyses of α-D-galactose (*a*) after origin shift and axial transformations, slope = 1·23, intercept = 0·01; (*b*) after least-squares fit of molecular parameters, slope = 0·91, intercept = −0·09.

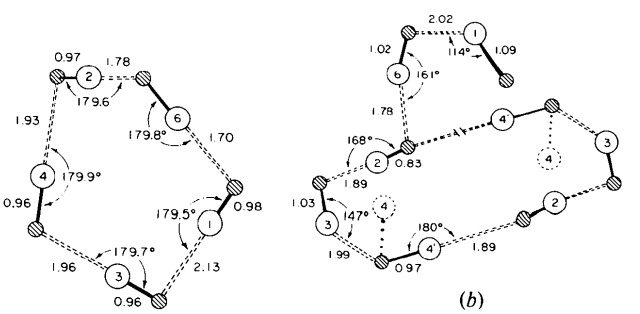
After appropriate axial and origin transformations, the agreement between the positional parameters for the C and O atoms is good, with the usual small underestimation of the standard deviations, as shown by the half-normal probability plot in Fig. 1(*a*). Slightly better agreement was obtained with the least-squares molecular best-fit program of Nyburg (1974), as shown by the plot in Fig. 1(*b*).

There are, however, large differences in the positions assigned to the H atoms which are attached to the O atoms, as shown in Fig. 2. This leads to important differences in the interpretation of the hydrogen-bond geometry which is shown in Fig. 3.



(*a*) (*b*)

Fig. 2. The molecular structure of α-D-galactose (*a*) according to (1), (*b*) according to (2).



(*a*) (*b*)

Fig. 3. Hydrogen-bonding geometry in the crystal structure of α-D-galactose (*a*) according to (1), (*b*) according to (2). Small circles are O atoms, large circles are H atoms. Solid lines, covalent O–H; dashed lines, hydrogen bond H···O. Full circle, H(4′) as determined in (1). Dotted circle, H(4) as determined in (2). ⟦ indicates that the link is to the molecule in the unit cell above, thereby forming an infinite chain.

In (1) the proposed hydrogen-bonding scheme consists of closed loops, with the donor–acceptor sequence:

$$\begin{array}{ccccc} O(6)H & \rightarrow & O(1)H & \rightarrow & O(3) \\ & \nwarrow & & & H \\ & & & & \downarrow \\ & & HO(2) & \leftarrow & HO(4) \end{array} .$$

The hydrogen bond H···O distances range from 1·70 to 2·13 Å, the longest being that from the anomeric hydroxyl O(1)H to O(3), and the shortest from O(6)H to the anomeric O(1). The O–H···O angles are exceptionally linear, ranging from 179·6 to 179·9° (a rather unlikely circumstance because of the well-known geometrical factor).

In (2) the position of one hydrogen, H(O4), was poorly defined and placed in an unlikely position which was only 1·797 Å from H(O3). A more reasonable position is that deduced from the structure (1) which places it close to the line between O(4) and O(2) at a hydrogen-bonding distance of 1·89 Å from O(2). The hydrogen-bond scheme for structure (2) consists of infinite chains with two-link side chains, *i.e.*

$$\begin{array}{ccccccccccc} \rightarrow & O(4)H & \rightarrow & O(2)H & \rightarrow & O(3)H & \rightarrow & O(4)H & \rightarrow & O(2)H & \rightarrow \\ & & & \uparrow & & & & & & & \\ & & & HO(6) & \leftarrow & HO(1) & & & & & \end{array} .$$

The H···O bond distances then span a narrower range, from 1·89 to 2·02 Å, and the O–H···O angles have values from 114 to 180°. The anomeric O(1)H···O(6) remains the longest hydrogen bond, making an unusually small O–H···O angle. The anomeric O is not a hydrogen-bond acceptor.

Our interest in this problem arises from the prediction by Tse & Newton (1977) and the observations by Jeffrey, Gress & Takagi (1977) and Jeffrey & Lewis (1977) that anomeric hydroxyls in simple pyranoses are generally strong hydrogen-bond donors, but very weak acceptors. The hydrogen-bonding proposed in (1) provided one of the few strong exceptions to this hypothesis, whereas that in (2) is in better agreement, especially if the true position for H(O1) is closer to the line between O(1) and O(6), thereby shortening the H···O bond distance. For this reason, we favor the hydrogen-bonding scheme (2). Final resolution of this question must come from a neutron diffraction study, which must await the growth of suitable crystals, an experiment which hitherto has been unsuccessful.

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