Glyceraldehyde; an *X*-Ray Study of DL-Glyceraldehyde Dimer

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Summary An *X*-ray study of DL-glyceraldehyde, dimerized by hemiacetal bondings, shows that the molecule has a chair-form symmetrical *p*-dioxan structure with all the hydroxy and hydroxymethyl groups bonded equatorially; the conformation is similar to that of β-D-glucopyranose.

Glyceraldehyde is the basic substance used in defining configuration, and is a fundamental aldotriose. The present *X*-ray investigation was undertaken in connexion with its conformational relationships with some aldoses previously analysed. Spectroscopic studies suggested the *p*-dioxan structure as the most plausible one for dimerized aldehydes.[1]

Single crystals of DL-glyceraldehyde dimer, $(C_3H_6O_3)_2$, obtained from a mixture of ethanol and ether after first dissolving the aldehyde in a small amount of water, are monoclinic; $a = 9{\cdot}479(9)$, $b = 6{\cdot}981(8)$, $c = 6{\cdot}409(6)$ Å, $\beta = 115{\cdot}74(8)°$; space group $P2_1/a$, $Z = 2$ (as a dimer).

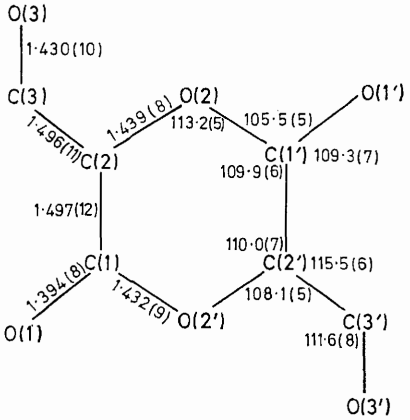

Figure 1.

The intensities of 684 independent reflexions were collected by visual estimation of Weissenberg photographs recorded with Cu-K_α radiation. The structure was solved by direct methods, in which the signs of 132 reflexions with $|E| > 1{\cdot}3$ were used for an E-map. Refinement of positional and thermal parameters by least squares reduced the R value to 0·130, assuming anisotropic thermal vibrations for carbon and oxygen atoms, and including hydrogen atoms located from a difference map.

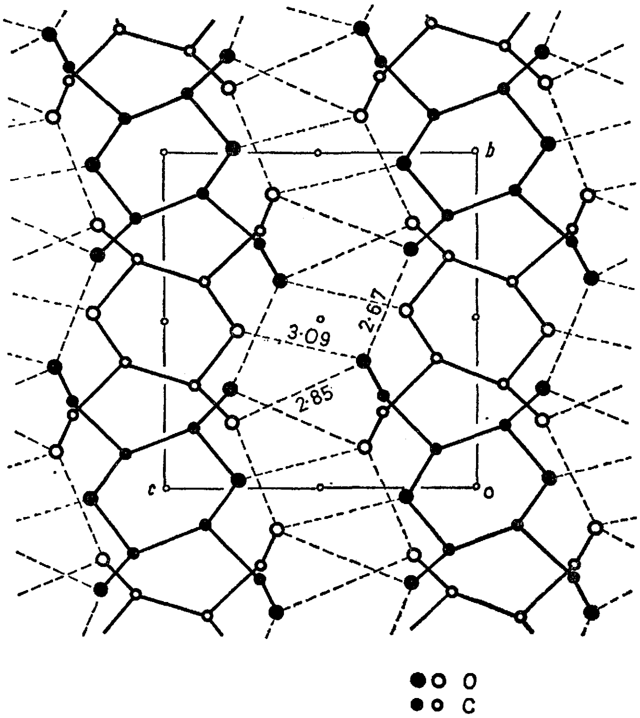

Figure 2.

The DL-glyceraldehyde, dimerized by hemiacetal bondings between the hydroxy and carbonyl groups of one monomer with another, has a chair-form symmetrical *p*-dioxan structure. The anomeric carbons C(1) and C(1′) have the β-configuration, and the exocyclic hydroxy and hydroxymethyl groups are equatorially bonded to the ring.

Though the C–C bond lengths are slightly shorter than is normal, the bond lengths and angles of this molecule (Figure 1) are similar to those of pyranose sugars. In particular the short length of the C(1)–O(1) bond and the small value of the O(2)–C(1′)–O(1′) angle agree with the general tendency of the equatorial anomeric C–O bonds.[2]

Torsion angles are: 56·1° for the mean value within the ring, 67·2° for O(1)–C(1)–C(2)–C(3) and −137·2° for O(1)–C(1)–C(2)–O(2), and 56·0° for C(1)–C(2)–C(3)–O(3) and −67·7° for O(2)–C(2)–C(3)–O(3); hence the conformation is *gauche-trans* around C(1)–C(2) and *gauche-gauche* around C(2)–C(3). The conformation around C(2)–C(3) with respect to the six-membered ring, agrees with one of the two preferred conformations of the exocyclic hydroxymethyl groups of pyranoses.[3] The partial structure around the hemiacetal bonds in this molecule is in good agreement with that of the corresponding part of β-D-glucose.[4]

Two kinds of hydrogen bonds having distances of 2·67 and 2·85 Å make up a spiral chain around a screw axis (see Figure 2); the former hydrogen bond links the molecules to the direction of the *b*-axis and the latter one is parallel to (20$\bar{1}$). Thus the crystal structure is made up from the molecular layers parallel to (20$\bar{1}$) with van der Waals interlayer distances. Within the layer there exists also another intermolecular approach of 3·09 Å between the ring oxygen and the oxygen of hydroxymethyl group, which may be interpreted as a bifurcated hydrogen bond.

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[4] S. S. C. Chu and G. A. Jeffrey, *Acta Cryst.*, 1968, **B24**, 830.