α-Glycerophosphate; an *X*-Ray Study of Disodium DL-α-Glycerophosphate Hexahydrate

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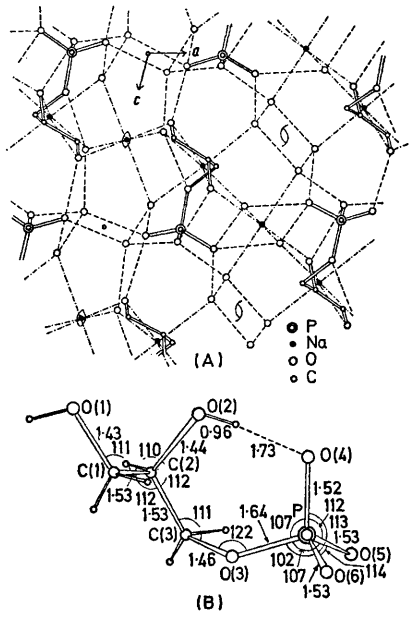
Summary An *X*-ray study of DL-α-glycerophosphate sodium salt shows that the α-glycerol residue has the *gauche–gauche* conformation and the presence of an intramolecular hydrogen bond between the β-hydroxy-group and an oxygen atom of the phosphate group.

α-GLYCEROPHOSPHATE (3-GP) is a biologically important intermediate in carbohydrate and phospholipid metabolism. The present *X*-ray investigation was undertaken in connection with its reaction mechanism. Single crystals of disodium DL-α-glycerophosphate hexahydrate, $C_3H_5(OH)_2$-$PO_4^{2-}Na_2^+$, $6H_2O$, from ethanol are monoclinic; $a = 24{\cdot}5$, $b = 8{\cdot}37$, $c = 13{\cdot}9$ Å, $\beta = 106{\cdot}0°$; space group $C2/c$, $Z = 8$.

Intensities of 2679 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 319 reflexions with $|E| > 1{\cdot}5$ were used for an *E*-map.[1] Refinement of positional and thermal parameters by least squares has converged to a discrepancy index of 0·10, assuming anisotropic thermal vibrations. All hydrogen atoms were located from a difference map.

The crystal structure projected along the *b*-axis is shown in the Figure (A). There are three kinds of sodium ions, each being six-co-ordinated (distorted octahedral) by water or 3-GP hydroxy-groups; the Na–O distances vary from 2·38 to 2·57 Å. The crystal structure is built up from chains of these octahedra and the complete hydrogen-bond network is formed between these chains. Distances involving hydrogen bonds distances range from 2·69 to 2·98 Å for O···O and from 1·73 to 2·06 Å for O···H. None of the oxygen atoms of the phosphate group is co-ordinated to the sodium ion, in contrast to β-glycerophosphate.[2] Each of three phosphate oxygen atoms accepts three hydrogen bonds, while the remaining ester oxygen accepts a weak hydrogen bond.

Bond lengths and angles are given in the Figure (B) (e.s.d.s. $<$ 0·008 Å for bond lengths and 0·7° for bond angles). None of the C–C or C–O bond lengths is significantly different from normal. Three of the P–O bond lengths except that including the ester oxygen are almost the same and they may be well explained by the two $d\pi$–$p\pi$-orbital theory of Cruickshank.[3] The P–O(3) bond length of 1·64 Å and the C(3)–O(3)–P angle of 121·5° are



FIGURE

comparable with those for ester oxygen in other phosphates.[4] The small value of 102·3° for the O(3)–P–O(6) angle is usual for *trans*-oxygen. Torsion angles around the C–C bonds are 47·7° for C(1)–C(2)–C(3)–O(3), 76·3° for O(2)–C(2)–C(3)–O(3), and 175·5° for O(1)–C(1)–C(2)–C(3); hence the conformation of the glycerol residue is *gauche–gauche* around C(2)–C(3) and *trans* around C(1)–C(2), similar to those in L-α-glyceryl phosphate choline[5] and in its cadmium chloride salt.[6] The torsion angle for C(2)–C(3)–O(3)–P (90·0°) is smaller than in other monoester phosphates,[7] and gives rise to the approach of 2·69 Å between O(2) and O(4) atoms and the formation of a strong intramolecular hydrogen bond between these oxygen atoms, the proton attached to O(2) lying almost on a straight line between O(2) and O(4). This intramolecular hydrogen bond and the aforementioned intermolecular hydrogen bond at the ester oxygen are rare in the phosphates reported hitherto, and suggest that such hydrogen bonds may play an important role in the reaction of 3-GP with ATP or fatty acids.

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