The Crystal and Molecular Structure of Dipotassium Phenyl Phosphate ($K_2C_6H_5PO_4,1\frac{1}{2}H_2O$)

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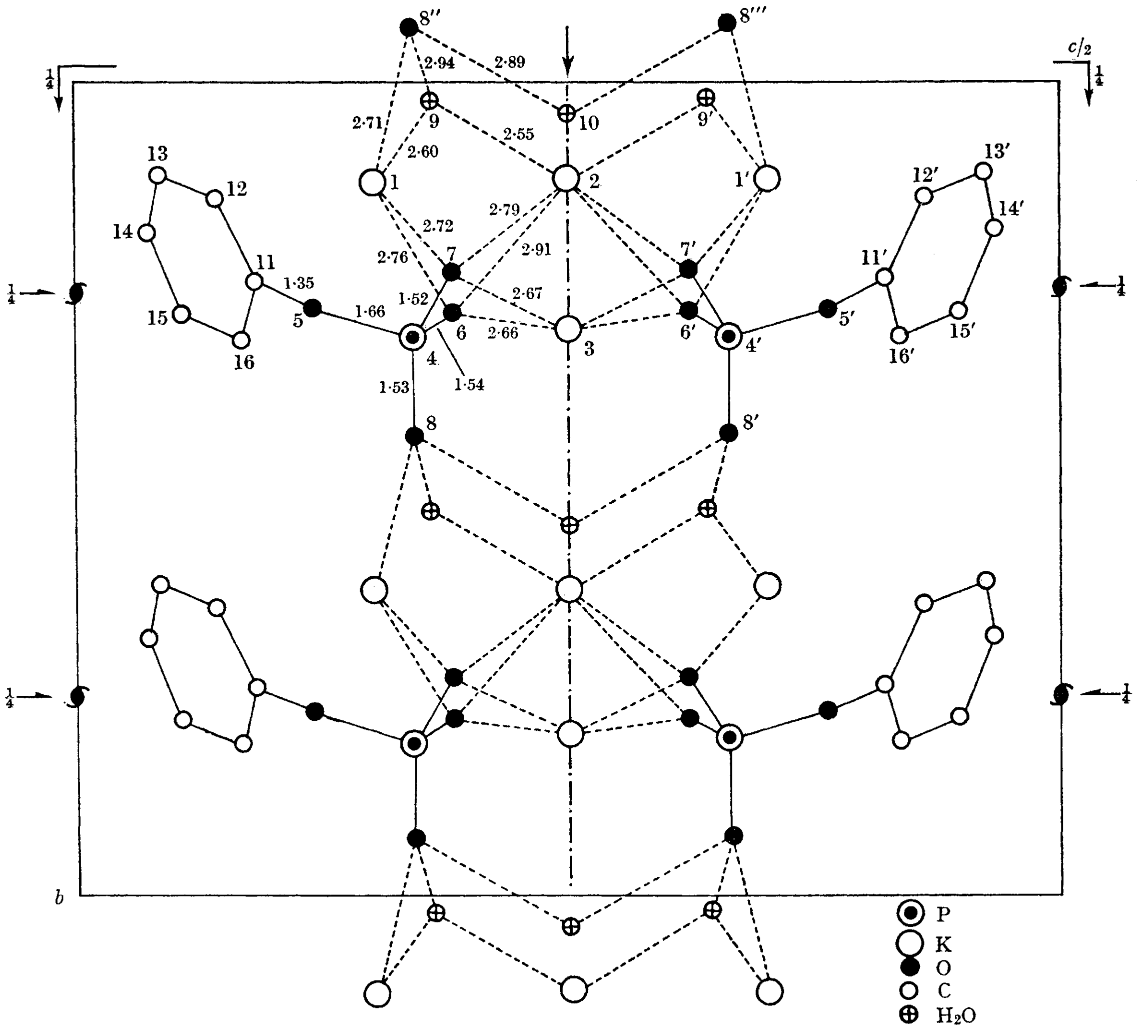
THE hydrolysis of organic phosphates has attracted considerable attention, particularly comparison of the rates and mechanisms of alkyl and aryl phosphates in acid and alkaline hydrolysis.[1,2] It is likely that the structures of these phosphates, in particular comparison of P–O–C linkages, will help in interpretation of the kinetic results, even though extrapolation from solid to solution is difficult. Furthermore, it has been shown that the presence of metal ions has an effect on the hydrolysis rates,[1] suggesting the possibility of a metal-ion complex solution. To explain the structural requirements for hydrolysis of monoesters the existence of a hydrogen-bonded complex between the monoanion, PO_4R^-, and a water molecule has also been postulated.[2] The effect of the hydrogen bonding and complex formation on P–O and PO–C distances may be significant in considering the various possibilities.

An X-ray study, using Cu-$K\alpha$ radiation, of a crystal of dipotassium phenyl phosphate enclosed in a capillary gave the following results:

$K_2C_6H_5PO_4,1\frac{1}{2}H_2O$ (F.W. = 277·24) *Orthorhombic*, a = 5·91, b = 12·01, c = 30·80 Å. U = 2186 Å^3, D_m = 1·735 g. cm.$^{-3}$, Z = 8, D_c = 1·683 g. cm.$^{-3}$ *Space group Pbcn* (No. 60).

The intensities of 720 photographically-recorded reflexions were estimated with a densitometer. No absorption corrections were made. After unsuccessful attempts to elucidate the Patterson functions, the structure was solved by the symbolic addition method.[3] It was refined by least-squares analysis, using isotropic vibrational parameters, to an R-value of 11%.

The structure, in its b-axial projection, is shown in the Figure. One K^+ ion is in a general position; two others, and one of the water molecules, are in



[100] Projection

FIGURE

special positions. If the limit of co-ordination is set at 3·0 Å, two of the K⁺ ions are four- and one is six-co-ordinated. An elaborate hydrogen-bonding scheme, along with this co-ordination, produces a tightly-knit structure. Some of the more important interatomic distances are shown in the Figure, their standard deviations being about 0·01 Å. The O–P–O angles range from 101° to 116°. Except for the one involved with the phenyl group, the three P–O bonds have the same length, and each of these three oxygen atoms makes three other bonded contacts, either to K^+ or by a hydrogen bond to H_2O.

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