1,2,3-Benzotriazolium Dihydrogen Phosphate, $[C_6H_4N_3H_2^+][H_2PO_4^-]$: *X*-Ray Crystal Structure reveals Very Strong Hydrogen Bonds

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1,2,3-Benzotriazole and H_3PO_4 produce crystals of a 1 : 1 adduct that has a structure composed of very short NHO and OHO hydrogen bonds linking the various ions and one oxygen atom in a unique chemical environment.

Among very strong hydrogen bonds, homonuclear ones such as FHF, OHO, and NHN are much more common than heteronuclear ones.[1,2] In particular NHO bonds, though encountered in many chemical and natural systems, are rarely strong. To qualify as very strong bonds should be 0.5 Å shorter than the sum of the van der Waals radii of oxygen and nitrogen, *i.e.* less than 2.55 Å.[1] To date no example of an NHO bond this short has been reported.

The shortest NHO bond reported so far is one of 2.600 Å in the pyridinium salt of 2-hydroxyphenyl phenylphosphonate which crystallised with the incorporation of catechol molecules of crystallisation.[3] We now report one of the same type (2.611 Å) in a much simpler system, 1,2,3-benzotriazolium dihydrogen phosphate. This salt, however, harbours other very strong hydrogen bonds between the phosphate entities, and these appear to be proton-centred hydrogen bonds.

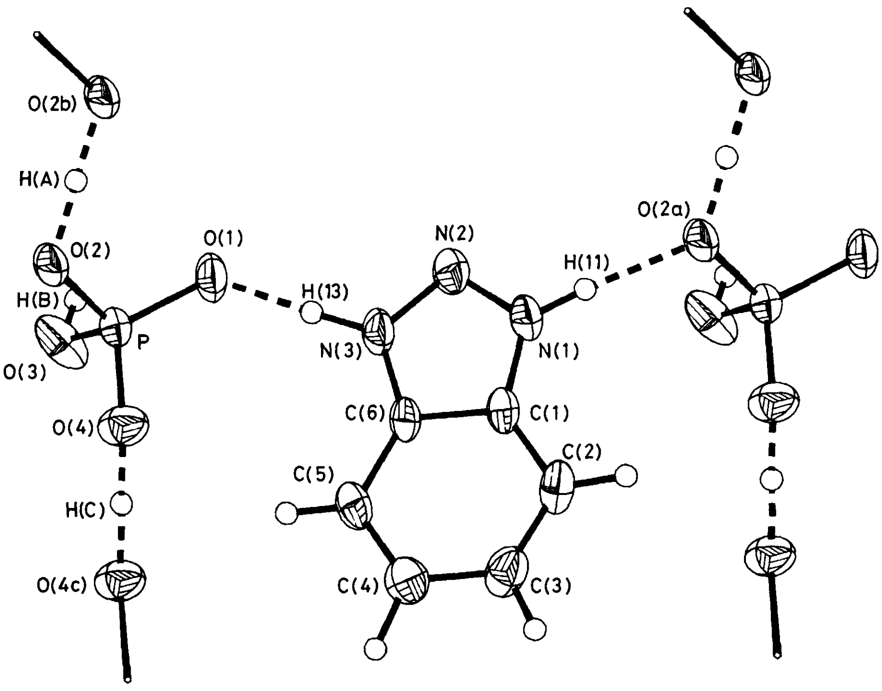

Figure 1. The structure of $[C_6H_4N_3H_2^+][H_2PO_4^-]$. Selected bond lengths (Å) are: N(1)–H(11) 0.943(30), N(1)–C(1) 1.365(3), N(1)–N(2) 1.317(3), N(2)–N(3) 1.314(3), N(3)–C(6) 1.364(3), C(1)–C(6) 1.390(3), N(3)–H(13) 1.019(27), P–O(1) 1.511(3), P–O(2) 1.545(3), P–O(3) 1.558(3), P–O(4) 1.510(3), O(2)–H(A) 1.242(2), O(4)–H(C) 1.225(2), hydrogen bonds: N(1) · · O(2a) 2.661, N(3) · · O(1) 2.611, O(1)–H(13) 1.593, O(2a)–H(11) 1.749; O(2) · · O(2b) 2.484, O(4) · · O(4c) 2.451. Symmetry operations relating designated atoms to reference atoms at (x, y, z): (a) $x, -1.0 + y, z$; (b) $-x, -y, -z$; (c) $1.0 -x, -y, 1.0 -z$.

Crystals were obtained from slow evaporation of an equimolar solution in methanol.

Figure 1† shows the hydrogen bonded network in which $H_2PO_4^-$ ions are linked to one another through centred hydrogen bonds of $R(O \cdot\cdot O) = 2.451$ and 2.484 Å in one direction, and to benzotriazolium cations *via* short NHO bonds of $R(N \cdot\cdot O) = 2.611$ and 2.661 Å in a perpendicular direction. The atom O(2a) is unique among oxygen atoms, forming as it does *two* very strong but very different hydrogen bonds.

The hydrogens H(A) and H(C) are both on centres of inversion at (0,0,0) and (½,0,½) respectively. The isotropic thermal parameter, U_{iso}, for H(C) is larger than those for H(A) and H(B), and may indicate that H(C) is undergoing some oscillation about the central position. No attempt was made to examine whether this is reflected in large anisotropy for the motion of H(C) since we do not feel that the accuracy of the data merits such treatment. It must be realised, however, that whatever the correct model is for the motion of H(C), the O(4) · · · O(4c) distance is still very short.

The hydrogen bonding of phosphorus acids and the phosphate group has recently been reviewed and attention drawn to a few phosphate–phosphate interactions held together by short bonds.[4] Strong phosphate-to-NH bonds are even rarer although many examples of weak POHN bonding are known with a range of bond lengths $R(N \cdot\cdot O)$ of 2.65—3.10 Å with an average of 2.84 Å.[4] In this respect the bond reported here is clearly in the very strong category.

The formal positive charge on the N–H bond is no doubt influential in producing the very short NHO bonds. Other systems of this kind with shorter bonds than expected have been reported: 1,2,3-benzotriazolium hydrogen sulphate (2.687, 2.705 Å);[5] $[Cu(C_3H_4N_2)_5][P(OPh)_3O] \cdot 4H_2O$, a copper-imidazolium complex (2.638, 2.777 Å);[6] imidazolium dihydrogen phosphate (2.712 Å)[7]; imidazolium trimethyl phosphate (2.67, 2.68 Å);[8] and 4-oxopyrido[1,2-*a*]pyrimidin-1-ium-2-olate (2.698 Å).[9] In view of the biochemical importance of heterocyclic and other $N–H^+$ units and the common occurrence of phosphates it would seem to be only a matter of time before very strong hydrogen bonding between the two is reported or speculated upon in a natural system. The substance reported in this communication provides the best example to date that simple systems can interact in this manner to form POHN bonds.

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† *Crystal data:* $C_6H_8N_3O_4P$, $[C_6H_4N_3H_2^+][H_2PO_4^-]$, $M = 217.12$, triclinic, $a = 7.8962(4)$, $b = 8.9683(4)$, $c = 6.6419(3)$ Å, $\alpha = 107.849(4)$, $\beta = 101.316(4)$, $\gamma = 81.907(4)°$, space group $P\bar{1}$, $U = 437.366$ Å^3, $D_c = 1.611$ g cm^{-3}, $Z = 2$, $\mu(Cu\text{-}K_\alpha) = 26.59$ cm^{-1}, $\lambda = 1.5418$ Å, $T = 20$ °C. Of 1662 unique reflections 1575 were used in the refinement $[I > 1.5\ \sigma(I)]$; $R = 0.0354$. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located in difference maps and refined freely with individual isotropic thermal parameters. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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