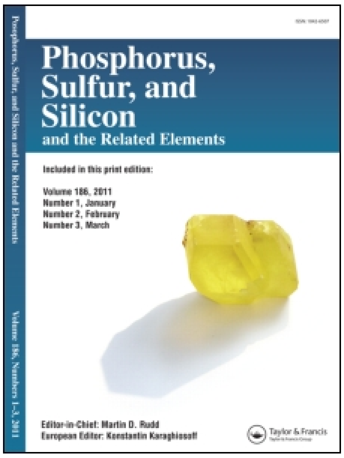

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VERY STRONG HYDROGEN BONDING OF PHOSPHATES: X-RAY CRYSTAL STRUCTURES OF 1,2,3-BENZOTRIAZOLIUM DIHYDROGEN PHOSPHATE $[C_6H_4N_3H_2^+][H_2PO_4^-]$ AND 1,3-BENZIMIDAZOLIUM DIHYDROGEN PHOSPHATE $[C_7H_5N_2H_2^+][H_2PO_4^-]$

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VERY STRONG HYDROGEN BONDING OF PHOSPHATES: X-RAY CRYSTAL STRUCTURES OF 1,2,3-BENZOTRIAZOLIUM DIHYDROGEN PHOSPHATE $[C_6H_4N_3H_2^+][H_2PO_4^-]$ AND 1,3-BENZIMIDAZOLIUM DIHYDROGEN PHOSPHATE $[C_7H_5N_2H_2^+][H_2PO_4^-]$

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1,2,3-Benzotriazole and 1,3-benzimidazole produce crystals of 1:1 adducts with H_3PO_4. Their X-ray structures reveal chains of phosphate ions linked through very short OHO hydrogen bonds. These chains are cross-linked through NHO hydrogen bonds to the 1,3-nitrogen atoms of the protonated bases. Although structurally similar, there are differences between the two systems—the benzotriazolium salt having shorter hydrogen bonds than the benzimidazolium salt. This is attributed not to their relvative basicities, but to crystal packing forces.

INTRODUCTION

The definitive work on the structure of phosphorus compounds[1] devotes a large section to the hydrogen bonding of the phosphate group. Most of the examples of interphosphate hydrogen bonds have $R(O\cdots O)$ in the range 2.50–2.65 Å but some examples are significantly shorter than this such as in di-p-chlorophenyl phosphate (2.398 Å)[2], and the adducts $NH_4H_2PO_4{\cdot}H_3PO_4$ (2.464 Å)[3] and $KH_2PO_4{\cdot}H_3PO_4$ (2.40 Å).[4] In a preliminary communication we have revealed another very short hydrogen bond between the dihydrogen phosphate ions of the 1,2,3-benzotriazolium salt.[5] However we find in the very similar lattice of the isoelectronic ion, the 1,3-benzimidazolium salt, the interphosphate hydrogen bonds are much longer. Both structures are now reported in full.

EXPERIMENTAL

Instruments I.r. spectrometer, Perkin-Elmer 983G [KBr discs]; X-ray diffractometers, Enraf-Nonius CAD4.

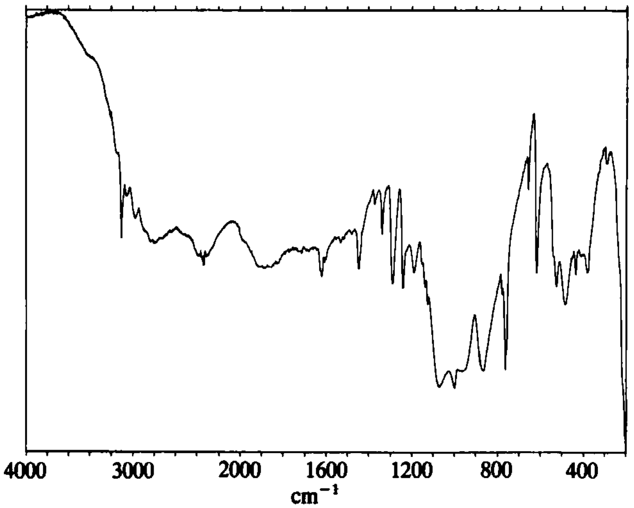


FIGURE 1 I.r. spectrum of $[C_6H_4N_3H_2^+][H_2PO_4^-]$ (A).

Preparation of 1,2,3-Benzotriazolium Dihydrogen Phosphate Colourless crystals were obtained by slow evaporation of a methanol solution of an equimolar mixture of 1,2,3-benzotrizole and H_3PO_4. M.pt. 109–111°C. Found: C, 33.33; H, 3.66; N, 19.68%. $C_6H_8N_3O_4P$ requires: C, 33.19; H, 3.71; N, 19.35%. I.r. spectrum, Figure 1.

Preparation of 1,3-Benzimidazolium Dihydrogen Phosphate Colourless crystals were obtained by slow evaporation of a methanol solution of an equimolar mixture of 1,3-benzimidazole and H_3PO_4. M.pt. 154–156°C. Found: C, 38.88; H, 4.25; N, 13.08%. $C_7H_9N_2O_4P$ requires: C, 38.90; H, 4.20; N, 12.96%. I.r. spectrum, Figure 2.

X-Ray Crystallography

All crystallographic measurements were made at room temperature on crystals sealed in glass capillianes, using the CAD4 diffractometer operating in the ω-2θ scan mode as previously described.[6]

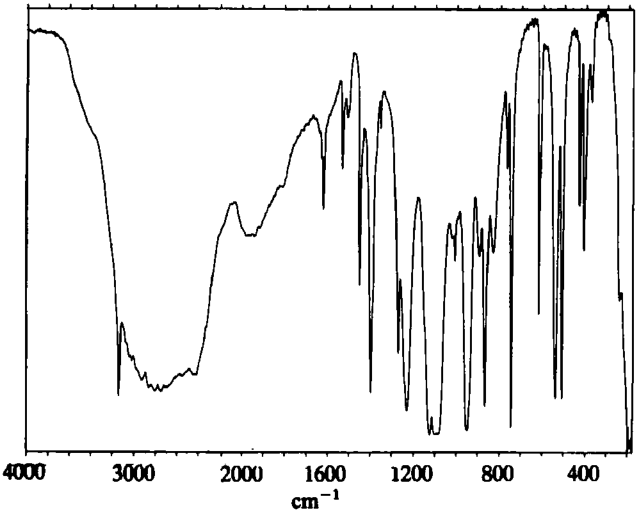


FIGURE 2 I.r. spectrum of $[C_7H_5N_2H_2^+][H_2PO_4^-]$ (B).

TABLE I

Fractional atomic co-ordinates (× 10^4) for $[C_6H_4N_3H_2^+][H_2PO_4^-]$

	x	y	z	$B_{exp}(Å)^2$
P	2006(1)	−45(1)	3258(1)	2.53(2)
0(1)	1134(2)	−1482(1)	3100(2)	3.02(5)
0(2)	1257(2)	580(2)	1311(3)	3.87(1)
0(3)	1674(2)	1289(2)	5322(3)	4.42(1)
0(4)	3946(2)	−310(2)	3340(2)	3.63(1)
N(1)	2616(2)	−6823(2)	1484(3)	3.00(1)
N(2)	1571(2)	−5522(2)	1723(3)	3.08(1)
N(3)	2572(2)	−4364(2)	2251(3)	2.68(1)
C(1)	4317(2)	−6522(2)	1893(3)	2.53(1)
C(2)	5874(3)	−7491(2)	1879(3)	3.32(1)
C(3)	7351(3)	−6724(3)	2386(3)	3.55(1)
C(4)	7315(3)	−5071(3)	2898(3)	3.24(1)
C(5)	5798(3)	−4121(2)	2917(3)	2.76(1)
C(6)	4283(2)	−4897(2)	2387(3)	2.29(1)
HA	0	0	0	6.40(13)*
HB	723(42)	1259(35)	5791(51)	5.84(9)*
HC	5000	0	5000	11.76(24)*
H(11)	2116(37)	7709(33)	1373(43)	5.05(8)*
H(13)	2049(33)	−3227(31)	2554(39)	4.18(7)*
H(2)	5817(30)	−8641(28)	1450(36)	3.47(6)*
H(3)	8503(3)	−7245(29)	2448(40)	4.34(7)*
H(4)	8511(31)	−4576(27)	3395(38)	3.79(6)*
H(5)	5784(27)	−2993(27)	3310(34)	3.16(6)*

* Starred atoms were refined isotropically.

Compound A

$C_6H_8N_3O_4P$, $[C_6H_4N_3H_2^+][H_2PO_4^-]$ $M = 217.12$, 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, $D_c = 1.611$ cm^{-3}, $Z = 2$, $\mu(Cu\text{-}K_\alpha) = 26.59$ cm^{-1}, $\lambda = 1.5418$ Å, $T = 20°C$, crystal dimensions 0.40 × 0.28 × 0.24 mm.

TABLE II

Bond lengths (Å) and angles (°) for $[C_6H_4N_3H_2^+][H_2PO_4^-]$

O(1)-P	1.511(3)	O(2)-P	1.545(3)
O(3)-P	1.558(3)	O(4)-P	1.510(3)
N(2)-N(1)	1.317(3)	C(1)-N(1)	1.365(3)
N(3)-N(2)	1.314(3)	C(6)-N(3)	1.364(3)
C(2)-C(1)	1.402(4)	C(6)-C(1)	1.390(3)
C(3)-C(2)	1.370(4)	C(4)-C(3)	1.414(4)
C(5)-C(4)	1.368(4)	C(6)-C(5)	1.400(4)
O(2)-P-O(1)	110.2(2)	O(3)-P-O(1)	110.2(2)
O(4)-P-O(1)	114.8(2)	O(3)-P-O(2)	107.8(2)
O(4)-P-O(2)	106.9(2)	O(4)-P-O(3)	106.6(2)
C(1)-N(1)-N(2)	111.8(3)	N(3)-N(2)-N(1)	106.1(3)
C(6)-N(3)-N(2)	111.7(2)	C(2)-C(1)-N(1)	133.0(2)
C(6)-C(1)-N(1)	104.9(3)	C(6)-C(1)-C(1)	122.1(3)
C(3)-C(2)-C(1)	115.4(3)	C(4)-C(3)-C(2)	122.5(3)
C(5)-C(4)-C(3)	122.3(3)	C(6)-C(5)-C(4)	115.5(3)
C(1)-C(6)-N(3)	105.4(3)	C(5)-C(6)-N(3)	132.3(2)
C(5)-C(6)-C(1)	122.3(3)		

TABLE III

Hydrogen bonds of $[C_6H_4N_3H_2^+][H_2PO_4^-]$

A—H··B(Å)	A—H(Å)	H··B(Å)	A··B(Å)
N(1)—H(11)··O(2)[a]	0.91(3)	1.75(3)	2.661(3)
N(3)—H(13)··O(1)	1.02(3)	1.59(3)	2.611(3)
O(2)—H(A)··O(2)[b]	1.24(2)	1.24(2)	2.484(3)
O(4)—H(C)··O(4)[c]	1.23(2)	1.23(2)	2.451(3)
O(3)—H(B)··O(1)	0.87(3)	1.73(3)	2.596(3)

Symmetry operations relating designated atoms to reference atoms at (x, y, z):

[a] $x,\ -1.0+y,\ z.$

[b] $-x,\ -y,\ -z.$

[c] $1.0-x,\ -y,\ 1.0-z.$

Intensities of 1662 unique reflections ($\theta_{max} = 60°$) were measured of which 1575 satisfied the criterion $I > 1.5\sigma(I)$ and were used in the structure solution by direct methods and refinement which proceeded by standard full-matrix least squares,[7] with unit weights assigned to each reflection. Corrections for absorption were applied. The final R value was 0.035. Table I gives the atomic coordinates, Table II the bond lengths and angles and Table III the hydrogen bond details. Figure 3 shows the structure and atom numbering and Figure 4 a section of the structure projected along the *a* axis.

Compound B

$C_7H_9N_2O_4P$, $[C_7H_5N_2H_2^+][H_2PO_4^-]$, $M = 216.13$, orthorhombic, $a = 7.785(4)$, $b = 10.077(2)$, $c = 24.148(7)$ Å, space group *Pcan* (non-standard form of no. 60), [standard form = *Pbcn*] $U = 1895(2)$ Å^3, $D_c = 1.516\ \mathrm{g\,cm^{-3}}$, $Z = 8$, $\mu(\text{Cu-K}_\alpha) = 25.65\ \mathrm{cm^{-1}}$, $\lambda = 1.5418$ Å, $T = 20°$C, crystal dimensions 0.32 × 0.26 × 0.15 mm.

The structure was solved by direct methods using MULTAN and refined by full-matrix least squares refinements of 1415 unique reflections ($\theta_{max} = 60°$) 1129 with $I > 1.5\ \sigma(I)$ were used in the refinement. All the hydrogen atoms were revealed in difference Fourier maps and their positional and isotropic thermal parameters were included in the refinements except for H6. All the non-hydrogen atoms were refined anisotropically. The final R factor was 0.037 with the maximum shift/error of 0.01. A final difference map did not show any peaks >0.20e/Å^3. Unit weight was assigned to each reflection. Absorption and extinction corrections were taken into account. Atomic scattering factors were taken from *International Tables for X-Ray Crystallography.*[8] Table IV lists the atomic coordinates, Table V the bond lengths and angles and Table VI the hydrogen bond details. Figure 5 shows the structures and atom numbering and Figure 6 the unit cell viewed along the *a* axis.

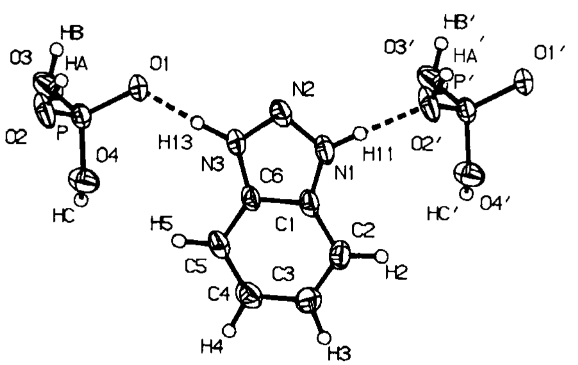


FIGURE 3 Structure and atom labelling of $[C_6H_4N_3H_2^+][H_2PO_4^-]$.

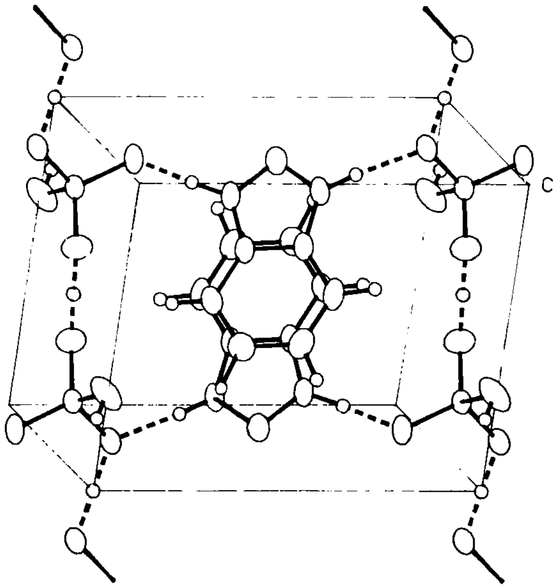


FIGURE 4 Section of the structure of [$C_6H_4N_3H_2^+$][$H_2PO_4^-$] projected along the *a* axis.

TABLE IV

Fractional atomic coordinates ($\times 10^4$) for [$C_7H_5N_2H_2^+$][$H_2PO_4^-$]

Atom	*x*	*y*	*z*	$B_{exp}(Å)^2$
P1	6014(1)	6866(8)	3323(3)	2.04(1)
O1	7562(3)	6104(2)	3513(1)	3.24(5)
O2	4635(3)	6078(2)	3040(1)	2.74(5)
O3	6546(3)	7978(2)	2901(9)	2.97(5)
O4	5295(3)	7596(3)	3843(9)	3.10(5)
N1	8751(4)	1456(3)	3316(1)	3.32(6)
N2	8207(4)	3530(3)	3473(1)	2.58(6)
C2	8901(4)	2681(4)	3124(1)	3.01(7)
C3	7584(4)	2844(3)	3920(1)	2.42(7)
C4	7919(4)	1509(3)	3823(2)	2.96(7)
C5	6765(5)	3270(4)	4399(2)	3.87(9)
C6	6359(5)	2279(7)	4771(2)	6.1(1)
C7	6737(6)	0941(5)	4663(2)	6.9(1)
C8	7502(6)	0534(4)	4194(2)	5.1(1)
HO3	7450(40)	8380(30)	2960(10)	3.3(8)*
HO4	4370(60)	8110(40)	3790(20)	7(1)*
HN1	9160(50)	670(40)	3170(20)	4.6(9)*
HN2	8070(40)	4380(30)	3460(10)	3.1(8)*
H2	9450(40)	2940(30)	2770(10)	3.8(8)*
H5	6550(40)	4280(30)	4440(10)	4.0(8)*
H6	5990	2500	5160	4.8(8)*
H7	6520(50)	310(40)	4870(20)	6(1)*
H8	7680(50)	−460(40)	4100(20)	5(1)*

* Starred atoms were refined isotropically.

TABLE V

Bond distances (Å) and angles (°) for $[C_7H_5N_2H_2^+][H_2PO_2^-]$

P-O(1)	1.501(2)	C(6)-C(7)	1.405(10)
P-O(2)	1.499(2)	C(7)-C(8)	1.345(7)
P-O(3)	1.569(2)	O(3)-4(03)	0.82(3)
P-O(4)	1.559(2)	O(4)-H(04)	0.90(4)
N(1)-C(2)	1.323(4)	N(1)-H(N1)	0.92(4)
N(1)-C(4)	1.387(4)	N(2)-H(N2)	0.86(3)
N(2)-C(2)	1.316(4)	C(2)-H(2)	1.00(3)
N(2)-C(3)	1.370(4)	C(5)-H(5)	1.04(4)
C(3)-C(4)	1.391(4)	C(6)-H(6)	0.99(4)*
C(3)-C(5)	1.389(4)	C(7)-H(7)	0.82(4)
C(4)-C(8)	1.368(5)	C(8)-H(8)	1.04(4)
C(5)-C(6)	1.380(6)		
O(1)-P-O(2)	116.3(1)	N(2)-C(3)-C(5)	131.5(3)
O(1)-P-O(3)	110.6(1)	C(4)-C(3)-C(5)	121.7(3)
O(1)-P-O(4)	106.5(1)	N(1)-C(4)-C(3)	105.8(3)
O(2)-P-O(3)	105.8(1)	N(1)-C(4)-C(8)	131.4(4)
O(2)-P-O(4)	111.0(1)	C(3)-C(4)-C(8)	122.8(4)
O(3)-P-O(4)	106.2(1)	C(3)-C(5)-C(6)	115.1(4)
O(2)-N(1)-C(4)	108.3(3)	C(5)-C(6)-C(7)	121.8(4)
C(2)-N(2)-C(3)	108.7(3)	C(6)-C(7)-C(8)	122.8(6)
N(1)-C(2)-N(2)	110.3(3)	C(4)-C(8)-C(7)	115.9(5)
N(2)-C(3)-C(4)	106.8(3)		

* Atomic parameters of H(6) were not refined.

TABLE VI

Hydrogen bonds of $[C_7H_5N_2H_2^+][H_2PO_4^-]$

A—H··B (Å)	A—H (Å)	H··B (Å)	A··B (Å)
N(1)—H(N1)··O(2)[a]	0.92(4)	1.83(4)	2.728(3)
N(2)—H(N2)··O(1)[b]	0.86(3)	1.79(3)	2.644(3)
O(3)—H(O3)··O(2)[c]	0.82(3)	1.80(3)	2.608(3)
O(4)—H(O4)··O(1)[d]	0.90(4)	1.75(4)	2.622(3)

Symmetry operations:
[a] $1/2+x,\ 1/2-y,\ z.$
[b] $x,\ y,\ z.$
[c] $1/2+x,\ 3/2-y,\ z.$
[d] $1/2+x,\ 1/2-y,\ z.$

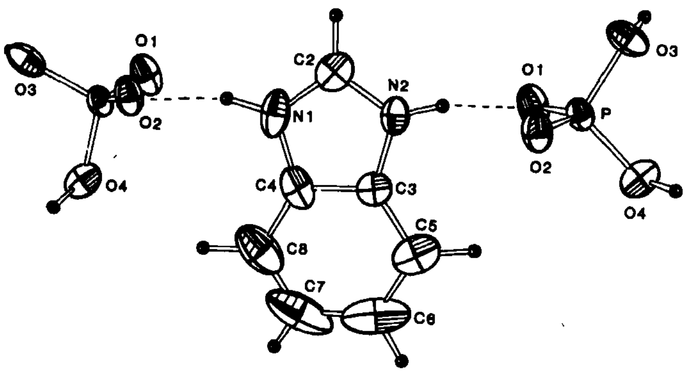


FIGURE 5 Structure and atom labelling of $[C_7H_5N_2H_2^+][H_2PO_4^-]$.

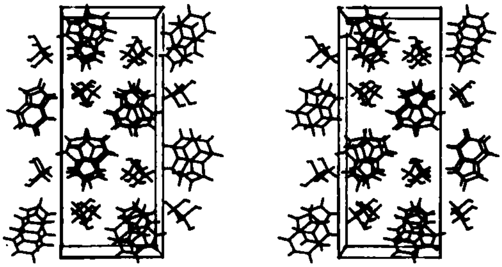


FIGURE 6 The unit cell of $[C_7H_5N_2H_2^+][H_2PO_4^-]$ viewed along the *a* axis.

DISCUSSION

In a preliminary communication[5] we reported the structure of $[C_6H_4N_3H_2^+]$ $[H_2PO_4^-]$ (A) with its unusual hydrogen bonding network and its chemically unique oxygen atom O(2a). This atom merits this title since it is the first example of an oxygen forming two very different but very strong hydrogen bonds. We now report fuller structural details of this salt, and in Figure 1 show its i.r. spectrum, which displays the characteristic absorptions of a very strongly hydrogen bonded system with broad bands centred at *ca* 2800, 2400, 1800 and 1600 cm^{-1}.

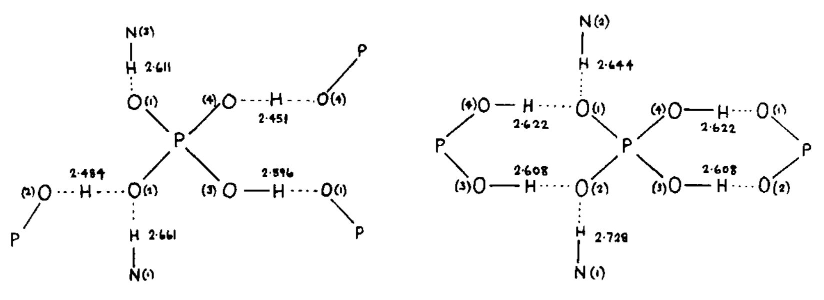
A similar 1:1 adduct can also be formed with 1,3-benzimidazole and H_3PO_4, $[C_7H_5N_2H_2^+][H_2PO_4^-]$ (B). The i.r. spectrum of this salt, Figure 2, is quite different in the region above 1500 cm^{-1}. The hydrogen bond stretching modes have moved to high frequencies which indicates weaker hydrogen bonding. This is borne out in the x-ray crystal structure. Although both (A) and (B) have essentially the same arrangament of chains of $[H_2PO_4^-]$ ions, linked by OHO hydrogen bonds and cross-linked by HNO hydrogen bonds to the protonated base, closer comparison of Tables III and VI shows that the hydrogen bonds are longer in (B) than in (A). This difference in behaviour might possibly stem from the very different basicities of the two bases: $pK_a(A) = 1.6$;[9] $pK_a(B)$ is 5.53.[10]

The two cations each form' two NHO hydrogen bonds and the lengths differ slightly in (B) but are very similar in (A). In a similar salt, $[C_6H_4N_3H_2^+][HSO_4^-]$. the N—H··O hydrogen bonds are 2.687 and 2.705 Å.[11] In this case, just as in (A), the cation has a plane of symmetry bisecting N2. 1,3-Benzimidazolium N—H··O hydrogen bonding, though somewhat longer at one side of the ion, is roughly comparable to that in (A) and if basicity is to be the explanation for the differences between (A) and (B) it is surprising that the N—H··O bonding does not reflect this. N—H··O bonding should be ≤2.60 Å to qualify as very short[12] and only one example has been so far reported, in the pyridinium salt of 2-hydroxyphenyl phenylphosphonate where R(N··O) = 2.600 Å.[13] A few examples are known with bonds slightly longer than this such as 2.63 Å of the nicotine-salicyclic acid complex,[14] and 2.64 Å of pentakis(imidazole)copper(II) monophenyl phosphate tetrahydrate.[15] The shorter NHO bond of (A) at 2.611 Å clearly shows it to be very strong compared to the majority of NHO hydrogen which generally exceed 2.80 Å even in the many N—H··O—P compounds known and Corbridge gives an average of 2.84 Å for 116 such bonds.[1] Even a bond of 2.728 Å, which is the longer bond in (B) stands comparison with other NHOP bonds that have been noted as short, such as the 2.71 Å bond of imidazolium dihydrogen phosphate,[16] and the 2.68 Å bond of imidazole-dimentyl phosphate.[17]

The PO · · H · · OP *hydrogen bonding*

In H_3PO_2 at −40°C the acid molecules are interlinked through short hydrogen bonds of $R(O\cdot\cdot O) = 2.44$ Å.[18] In H_3PO_4 the bonds are longer (2.53 Å)[19] but some phosphates have shorter bonds as in KH_2PO_4 (2.49 Å)[20] and $NH_4H_2PO_4$ (2.48 Å).[21] The salt-acid adduct $KH_2PO_4{\cdot}H_3PO_4$ has the shortest interphosphate bond (2.40 Å),[22] in line with other acid-conjugate base pairs.[12] In the compounds (A), and (B) the hydrogen bonding is between $H_2PO_4^-$ ions. In (A) the shortest $R(O\cdot\cdot O)$ is 2.451 Å which is shorter than either example quoted above. In (B) the shortest $R(O\cdot\cdot O)$ is 2.608 Å which is significantly different and typical of most PO · · H · · OP that Corbridge lists[1] where 53 examples have an average $R(O\cdot\cdot O)$ of 2.563 Å. Although both (A) and (B) consist of chains of hydrogen bonded $[H_2PO_4^-]$ ions, closer inspection shows the hydrogen bonding to be very different. (B) clearly has two phosphate oxygens acting as OH donors and two oxygens acting as acceptors—see Figure 7. And even though there is the usual uncertainty in locating the protons the P—O distances reflect which kind of oxygen each is. The non-protonated oxygens also act as acceptors for the N—H hydrogen bonds of the crosslinking benzimidazolium ions.

In (A) the P—O bond lengths give less information with only P—O(3) at 1.558 Å being identified as carrying a proton. The P—O(3)—H · · O(1) hydrogen bond at 2.596 Å is the weakest and clearly like the hydrogen bonds in (B). Two of the other oxygens participate in strong hydrogen bonds with the protons appearing to be centred. One of these P—O(2) bonds is also involved in hydrogen bonding to the cation. The fourth oxygen is not involved in OHO hydrogen bonding but only NHO. Consequently it appears that the crystal packing forces have determined the nature of the hydrogen bonded network and not the basicity of the organic base.



$[C_6H_4N_3H_2^+][H_2PO_4^-]$ (A)

$[C_7H_5N_2H_2^+][H_2PO_4^-]$ (B)

FIGURE 7 The hydrogen bonding environments of the phosphates.

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