A Novel Class of Salts for Second Harmonic Generation

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A new class of hydrogen-bonded dihydrogenphosphate salts, [AH][H_2PO_4] [where A = piperidine, 3-hydroxypyridine, 4-hydroxypyridine, 3-hydroxy-6-methylpyridine, 2,4,6-trimethylpyridine, benzylamine ($PhCH_2NH_2$), phenethylamine ($PRCH_2CH_2NH_2$), or 3-aminopropene], has been synthesized and demonstrated to exhibit second harmonic generation; the crystal structures of [$C_5H_{10}NH_2$][H_2PO_4] and [$C_6H_5CH_2NH_3$][H_2PO_4] are reported.

In recent years, materials possessing non-linear optical properties, notably those exhibiting second harmonic generation (SHG), have received considerable attention due to their wide-ranging applications (*e.g.* analysis of short pulses, optical mixers, conversion of wavelengths from the IR to the UV, *etc.*).[1,2] The known compounds exhibiting SHG are conveniently divided into two classes; inorganic salts and oxides [*e.g.* lithium niobate(v), potassium dihydrogenphosphate, and barium titanate(iv)][3,6] and organic molecules (*e.g* 3-nitroaniline, and 2-methyl-4-nitroaniline).[1,7—9] Unfortunately, various factors are hampering the efficiency of materials from both of these classes. Inorganic compounds usually suffer from degradative photoreactive effects, restricted birefringence, and limited solubility. Organic molecules are, potentially, more versatile due to larger β-values (the second-order molecular polarization coefficient), higher resistance to optical damage, and the possibilities of designing molecules highly suitable for SHG, *e.g.* combining large polarizability with the presence of substituents capable of charge transfer.[9] However, even though many organic molecules have very high β-values, their $\chi^{(2)}$-value (the second-order polarization coefficient for the medium) is often very small, since a high β-value is, usually, accompanied by a high dipole moment for the molecule: this encourages the molecules to form pairs aligned in an antiparallel fashion, thus favouring centrosymmetric crystal forms, and thereby ruling out the possibility of SHG-activity.[10] If highly polarizable organic molecules, with large second-order coefficients, could be prevented from forming unfavourable crystalline structures, their full potential could then be utilized.

We have therefore designed a new range of salts, combining a cation derived from a polarizable organic molecule (*e.g.* 2-hydroxypyridine, triphenylamine, or 2-aminopyrimidine), with an inorganic anion, dihydrogenphosphate, capable of

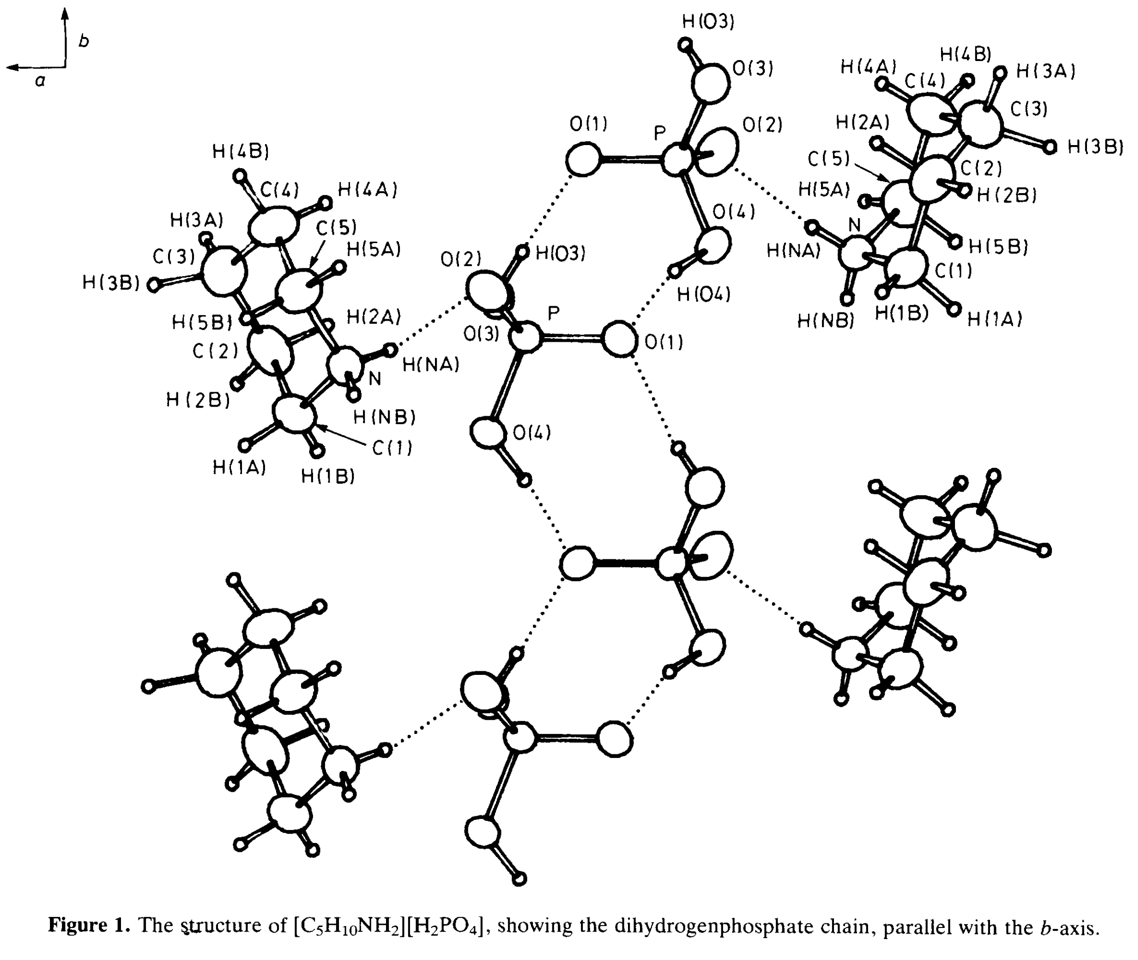

Figure 1. The structure of [$C_5H_{10}NH_2$][H_2PO_4], showing the dihydrogenphosphate chain, parallel with the *b*-axis.

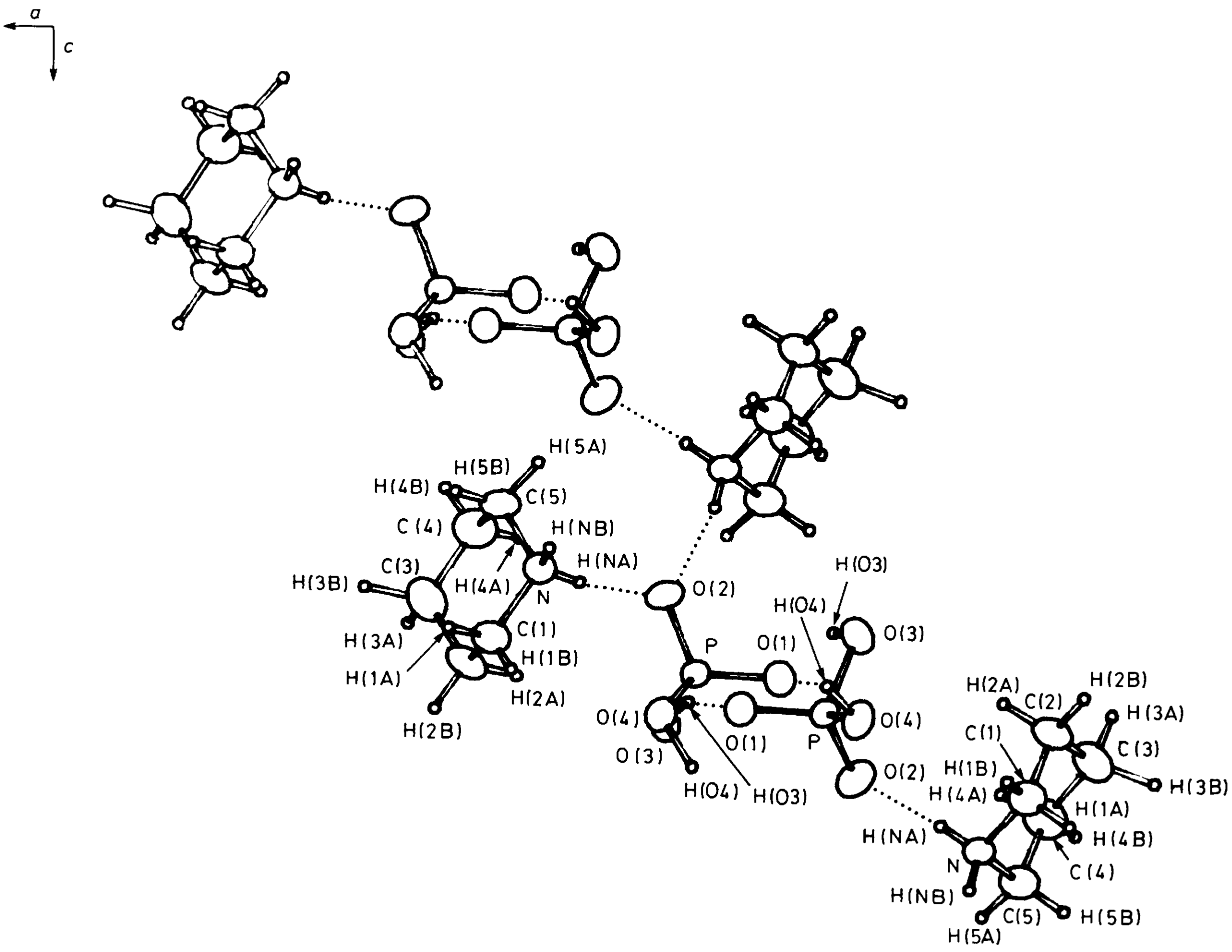

Figure 2. The structure of $[C_5H_{10}NH_2][H_2PO_4]$, showing the cross-linking in the *a–c* plane.

Table 1. SHG activity of selected organic dihydrogenphosphate salts.

Compound	Powder efficiency[a]
$[C_5H_{10}NH_2][H_2PO_4]$	0.9
$[2,4,6\text{-}Me_3C_5H_2NH][H_2PO_4]$	0.2
$[HO\text{-}3\text{-}C_5H_4NH][H_2PO_4]$	0.4
$[HO\text{-}4\text{-}C_5H_4NH][H_2PO_4]$	5.0
$[HO\text{-}3\text{-}Me\text{-}6\text{-}C_5H_3NH][H_2PO_4]$	0.8
$[PhCH_2NH_3][H_2PO_4]$	0.9
$[PhCH_2CH_2NH_3][H_2PO_4]$	0.6
$[CH_2{=}CHCH_2NH_3][H_2PO_4]$	0.4

[a] On a scale where α-SiO_2 is 1.0.

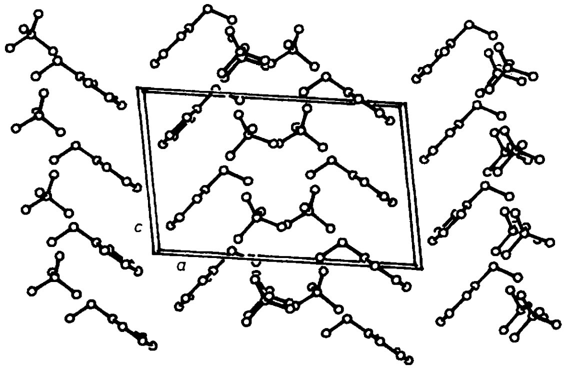

Figure 3. The 'herring-bone' packing of the phenyl groups in the *a–c* plane of $[PhCH_2NH_3][H_2PO_4]$.

forming strong hydrogen-bonded crystal structures. The bonding energy present in the hydrogen bonds can counteract the tendencies of the organic dipoles to form pairs, and drive the formation of salts with both high β *and* high $\chi^{(2)}$-values. The only known compound of this type is L-argininium dihydrogenphosphate monohydrate, $[(H_2N)_2CNH(CH_2)_3\text{-}CH(NH_3)CO_2][H_2PO_4]\cdot H_2O$.[11]

In initial studies, 24 salts of formula $[AH][H_2PO_4]$ (A = primary, secondary, or tertiary amine, *e.g.* 3-nitroaniline, 4-aminopyridine, or 3,5-dimethylpyrazole) were prepared and screened for SHG-activity, using the powder technique developed by Kurtz and Perry,[12] as described elsewhere.[13] The sample was placed between two clean glass slides and irradiated at 1064 nm, using a Nd:YAG laser: the 532 nm radiation could be observed visually. Of the samples tested, the dihydrogenphosphate salts of the following amines showed SHG-activity; piperidine, 3-hydroxypyridine, 4-hydroxypyridine, 2,4,6-trimethylpyridine, 3-hydroxy-6-methylpyridine, benzylamine ($PhCH_2NH_2$), phenethylamine ($PRCH_2CH_2NH_2$), and 3-aminopropene. Quantitative SHG measurements, relative to a powdered standard of α-SiO_2, were carried out on powdered samples of uniform thickness and particle size (Table 1). There is every reason to anticipate that these represent only a small fraction of the total number of SHG-active materials in this class of salts.

Table 2. Geometry of the hydrogen-bonds in $[C_5H_{10}NH_2][H_2PO_4]$.

D–H · · · A^9	r(D–H)/nm	r(H · · · A)/nm	r(D · · · A)/nm	(D–H · · · A)∠/°
N–H(NA) · · · O(2)$'$	0.084(3)	0.192(3)	0.2749(4)	168(4)
N–H(NB) · · · O(2)$''$	0.081(5)	0.192(5)	0.2709(4)	165(4)
O(3)–H(O3) · · · O(1)$'''$	0.079(6)	0.191(6)	0.2630(4)	151(6)
O(4)–H(O4) · · · O(1)$''''$	0.111(5)	0.152(5)	0.2568(4)	153(5)

[a] Symmetry codes: ($'$) x,y,z; ($''$) $1 - x, y - 1/2, \bar{z}$; ($'''$) $\bar{x}, y + 1/2, \bar{z}$; ($''''$) $\bar{x}, y - 1/2, \bar{z}$.

Table 3. Geometry of the hydrogen-bonds in $[PhCH_2NH_3][H_2PO_4]$.

D–H · · · A^a	r(D–H)/nm	r(H · · · A)/nm	r(D · · · A)/nm	(D–H · · · A)∠/°
N(1)–H(1a) · · · O(8)$'$	0.110(10)	0.173(10)	0.2806(7)	165(7)
N(1)–H(1b) · · · O(3)	0.082(9)	0.208(9)	0.2887(6)	168(7)
N(1)–H(1c) · · · O(2)$''$	0.102(8)	0.189(9)	0.2818(6)	149(6)
N(2)–H(2a) · · · O(4)$'''$	0.102(10)	0.181(9)	0.2795(6)	160(9)
N(2)–H(2b) · · · O(6)	0.082(9)	0.207(9)	0.2872(6)	169(7)
N(2)–H(2c) · · · O(7)$''''$	0,105(8)	0.181(8)	0.2819(6)	159(7)

[a] Symmetry codes: ($'$) $x, \bar{y}, 1/2 + z$; ($''$) $x, -1 + y, z$; ($'''$) $x, 1 - y, 1/2 + z$; ($''''$) $x, 1 + y, z$; ($'''''$) $x, 1 - y, -1/2 + z$; ($''''''$) $x, \bar{y}, -1/2 + z$.

In order to provide a clear view of the effects of hydrogen-bonding on the structure, X-ray structural analysis determinations† of these SHG-active salts have been initiated. Translucent crystals of piperidinium dihydrogenphosphate, $[C_5H_{10}NH_2][H_2PO_4]$, were grown from methanol.† The structure is characterized by infinite chains of $[H_2PO_4]^-$ units, linked, along the screw axis, by two of the four hydrogen bonds, O(3) · · · O(1)$'''$ and O(4) · · · O(1)$''''$ (Figure 1, Table 2) and cross-linked by the organic cation (Figure 2), clearly demonstrating the significant structural role of the hydrogen bond.

Translucent crystals of benzylammonium dihydrogenphosphate, $[PhCH_2NH_3][H_2PO_4]$, were grown from an aqueous solution.† The crystal structure consists of bilayers forming sheets parallel to the b–c plane. For convenience, when describing the structure, the phosphate groups will be referred to as P(1) and P(2), and the cations as N(1) and N(2). For each bilayer, the phosphate groups and the amino groups of the cations are near the centre of the bilayer, with the phenyl groups on the outside. Adjacent bilayers are arranged so as to give the characteristic 'herring-bone' packing of the phenyl groups (Figure 3). The N(1) and P(1) atoms are in a plane on one side of the centre of the bilayer, and the N(2) and P(2) atoms are in a parallel plane on the other side of the bilayer (Figure 4). Each NH_3^+ group forms two hydrogen bonds within the plane to oxygen atoms of $[H_2PO_4]^-$ groups related by a unit translation along the b axis, and one hydrogen bond to an oxygen atom of the phosphate group in the other plane (see Table 3). Each $[H_2PO_4]^-$ group also forms two hydrogen bonds within one side of the bilayer, linking O(1) to O(2)$'''''$ [0.2553(6) nm] and O(5) to O(7) [0.2571(6) nm] parallel to the c axis, and two more across the bilayer, linking O(4) to O(8)$''''''$ [0.2440(6) nm] and O(3) to O(6) [0.2506(6) nm] (see footnotes to Table 3 for symmetry codes). Clearly, as with the previous structure, the extensive

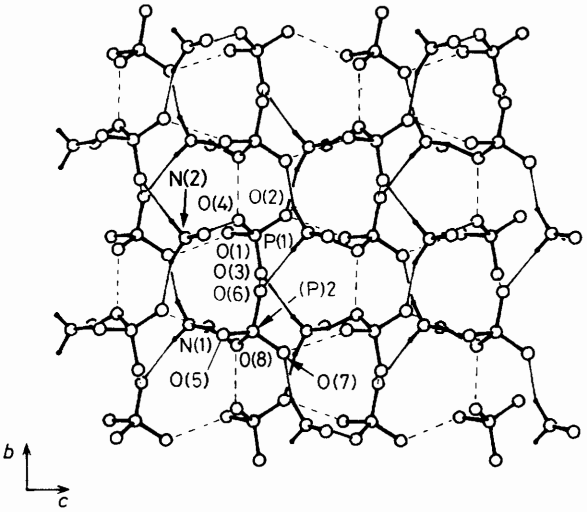

Figure 4. A view of the complex hydrogen bonding network in the b–c plane of $[PhCH_2NH_3][H_2PO_4]$.

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† *Crystal data:* $C_5H_{14}NO_4P$, M = 183.2, monoclinic, space group $P2_1$, a = 0.8385(2), b = 0.6227(2), c = 0.8836(4) nm, β = 112.43(3)°, U = 0.4264 nm^3, Z = 2, D_c = 1.43 g cm^{-3}, μ(Mo-K_α) = 12.4 cm^{-1}, crystal dimensions = 0.32 × 0.28 × 0.25 mm. 878 unique reflections were measured for $2 < \theta < 25°$, and 761 significant reflections were used in the refinement. The final residuals were R = 0.035, R_w = 0.044. *Crystal data*: $C_7H_{12}NO_4P$, M = 205.2, monoclinic, space group Pc, a = 1.4744(5), b = 0.7130(3), c = 0.9116(7) nm, β = 99.18(4)°, U = 0.9461 nm^3, Z = 4, D_c = 1.44 g cm^{-3}, μ(Mo-K_α) = 2.7 cm^{-1}, crystal dimensions = 0.50 × 0.30 × 0.10 mm. 1916 unique reflections were measured for $2 < \theta < 25°$, and 1288 significant reflections were used in the refinement. The structures were solved by direct methods and refined with non-hydrogen atoms anisotropic, hydrogen atoms of the cation refined isotropically. The phosphate anion showed a small occupancy (25%) of an alternative orientation, and its hydrogen atoms could not be located. The final residuals were R = 0.045, R_w = 0.055. All crystallographic data were recorded on an Enraf-Nonius CAD4 diffractometer. No correction was made for absorption. Refinement was by full matrix least-squares, with weighting scheme $w = \sigma^{-2}(F)$, using reflections with $I > \sigma(I)$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

network of hydrogen bonds plays a key role in determining the packing and geometry of the crystal.

One of the key advantages of the organic dihydrogenphosphate salts is their solubility compared with $BaTiO_3$, $LiNbO_3$, *etc.* This has enabled the incorporation of $[C_5H_{10}NH_2]$-$[H_2PO_4]$ into an organic polymer, poly(vinylalcohol), resulting in a SHG-active composite. Moreover, in contrast to the recently reported organometallic derivative, *cis*-1-ferrocenyl-2-(4-nitrophenyl)ethene,[14] these salts are transparent in the visible region.

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