Crystal structure of 4-phenylbutylammonium dihydrogenphosphate, $[C_6H_5(CH_2)_4NH_3)](H_2PO_4)$

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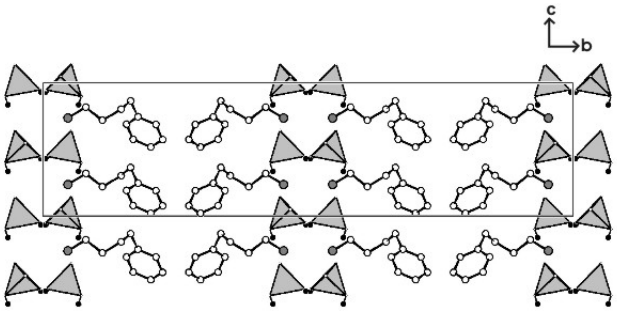

Abstract

$C_{10}H_{18}NO_4P$, orthorhombic, *Aba*2 (no. 41), $a = 7.218(1)$ Å, $b = 36.600(7)$ Å, $c = 9.188(2)$ Å, $V = 2427.2$ Å^3, $Z = 8$, $R_{gt}(F) = 0.043$, $wR_{ref}(F^2) = 0.105$, $T = 296$ K.

Source of material

A hydrothermal reaction was carried out in a 23 ml Teflon-lined stainless steel Parr hydrothermal reaction vessel at 150 °C for 2 d. Phosphoric acid (0.03 ml, 0.5 mmol), 4-phenyl-butylamine (0.24 ml, 1.5 mmol), and water (3.0 ml) were allowed to react. The pH value of the solution before and after the reaction was 11.3 and 7.5, respectively. The solid products were recovered by vacuum filtration and washed with water. Colorless platy crystals suitable for analysis were obtained. The yield of the crystalline product was ~40 % based on phosphorous.

Experimental details

Hydrogen atoms were placed in calculated positions and refined as riding except those of the hydroxyl group in $H_2PO_4^-$ which were located in difference Fourier maps, and their positions and isotropic displacement parameters were refined. The Flack parameter was –0.03(15).

Discussion

The KH_2PO_4 (KDP) family is one of the most important classes in non-linear optics and ferroelectrics due to its non-centrosymmetric structure [1,2]. Many KDP analogues have been reported, and the arrangement of $H_2PO_4^-$ can be controlled by the species of counter cations incorporated in the structure [3-7]. A hydrogen bond between the counter cations and dihydrogenphosphate anions is a key variable to construct a non-centrosymmetric array of $H_2PO_4^-$ with very short O···O distances.

The title crystal structure is built up from a 4-phenylbutylammonium cation and a dihydrogenphosphate anion. The detailed analysis of $H_2PO_4^-$ confirms the positions of oxo- and hydroxyl groups by comparing the bond distances and angles, *i.e.*, *d*(P—O) of 1.4942(2) Å and 1.5369(3) Å are shorter than *d*(P—OH) of 1.5396(2) Å and 1.5647(2) Å, and ∠O–P–O = 114.2(2)° is wider than ∠HO–P–OH = 109.0(1)°. Each anion $H_2PO_4^-$ is strongly hydrogen bonded to one another forming "macroanionic" layers perpendicular to [010] (*d*(O···O) of 2.4979(5) Å and 2.5960(4) Å) [8]. The dipole moment of $H_2PO_4^-$ is partially cancelled, and the net dipole is oriented to [001], expecting ferrielectric properties. The 4-phenylbutylammonium cations are hydrogen bonded to $H_2PO_4^-$ layers through N–H···O interaction (*d*(N···O) = 2.8095(5) Å, 2.8240(4) Å, and 2.8979(4) Å). The 4-phenylbutylammonium cations form a bilayer arrangement between the dihydrogen phosphate layers.

Table 1. Data collection and handling.

Crystal:	colorless plate, size 0.04 × 0.10 × 0.34 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.26 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID, φ/ω
$2\theta_{max}$:	54.9°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11402, 2767
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2315
$N(param)_{refined}$:	154
Programs:	SHELXS-97, SHELXL-97 [9], DIAMOND [10]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	8*b*	0.082(5)	0.495(1)	–0.067(4)	0.06(2)
H(2)	8*b*	0.261(5)	0.4335(8)	–0.164(3)	0.021(8)
H(1A)	8*b*	0.1856	0.0443	0.1663	0.052
H(1B)	8*b*	0.2618	0.0274	0.2962	0.052
H(1C)	8*b*	0.3823	0.0474	0.1979	0.052
H(1D)	8*b*	0.3433	0.0865	0.3760	0.041
H(1E)	8*b*	0.1328	0.0762	0.3871	0.041
H(2A)	8*b*	0.0746	0.1060	0.1664	0.046
H(2B)	8*b*	0.2855	0.1156	0.1513	0.046
H(3A)	8*b*	0.0707	0.1422	0.3843	0.059
H(3B)	8*b*	0.0944	0.1646	0.2403	0.059
H(4A)	8*b*	0.2973	0.1849	0.4295	0.062
H(4B)	8*b*	0.3982	0.1469	0.4235	0.062
H(6)	8*b*	0.6209	0.1343	0.2294	0.064
H(7)	8*b*	0.7998	0.1552	0.0402	0.080
H(8)	8*b*	0.7490	0.2111	–0.0593	0.087
H(9)	8*b*	0.5261	0.2487	0.0381	0.086
H(10)	8*b*	0.3399	0.2280	0.2268	0.067

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	8*b*	0.24847(9)	0.45901(2)	0.01647(9)	0.0199(2)	0.0330(3)	0.0226(2)	–0.0019(3)	0.0006(2)	–0.0002(3)
O(1)	8*b*	0.1392(3)	0.44650(6)	0.1453(2)	0.032(1)	0.051(1)	0.0224(9)	–0.0002(9)	–0.0001(8)	0.0073(9)
O(2)	8*b*	0.1707(3)	0.49443(6)	–0.0501(2)	0.020(1)	0.040(1)	0.043(1)	0.004(1)	0.0019(9)	0.009(1)
O(3)	8*b*	0.4535(3)	0.46674(6)	0.0494(2)	0.0222(9)	0.040(1)	0.053(1)	0.0011(8)	–0.0064(8)	0.0040(9)
O(4)	8*b*	0.2382(4)	0.42782(6)	–0.0997(2)	0.059(2)	0.040(1)	0.025(1)	–0.006(1)	0.007(1)	–0.0021(9)
N(1)	8*b*	0.2694(3)	0.04649(6)	0.2368(2)	0.029(1)	0.044(1)	0.030(2)	–0.002(1)	0.001(1)	0.0034(9)
C(1)	8*b*	0.2340(4)	0.08036(8)	0.3197(3)	0.031(2)	0.043(2)	0.027(1)	0.001(1)	0.002(1)	0.002(1)
C(2)	8*b*	0.1858(4)	0.11197(9)	0.2207(3)	0.037(2)	0.045(2)	0.034(1)	–0.003(1)	–0.003(1)	0.003(1)
C(3)	8*b*	0.1547(5)	0.1472(1)	0.3042(4)	0.046(2)	0.048(2)	0.054(2)	0.005(2)	0.008(1)	0.001(2)
C(4)	8*b*	0.3315(5)	0.1648(1)	0.3658(4)	0.066(2)	0.049(2)	0.040(2)	0.001(2)	0.001(2)	–0.007(2)
C(5)	8*b*	0.4569(4)	0.17898(9)	0.2472(3)	0.046(2)	0.042(2)	0.038(2)	–0.006(1)	–0.005(1)	–0.006(2)
C(6)	8*b*	0.5988(5)	0.1574(1)	0.1904(4)	0.054(2)	0.051(2)	0.056(2)	0.008(2)	–0.011(2)	–0.002(2)
C(7)	8*b*	0.7061(6)	0.1699(1)	0.0772(5)	0.042(2)	0.082(3)	0.076(3)	–0.002(2)	0.003(2)	–0.011(2)
C(8)	8*b*	0.6777(6)	0.2032(1)	0.0189(6)	0.056(2)	0.089(3)	0.072(2)	–0.023(2)	0.008(3)	0.001(3)
C(9)	8*b*	0.5434(7)	0.2254(1)	0.0755(5)	0.080(3)	0.055(2)	0.081(3)	–0.013(2)	–0.003(2)	0.023(2)
C(10)	8*b*	0.4321(6)	0.2129(1)	0.1896(4)	0.059(2)	0.046(2)	0.064(2)	0.004(2)	–0.006(2)	–0.007(2)

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