organic compounds

Ethyl [(*n*-butylammonio)(2-hydroxyphenyl)methyl]phosphonate

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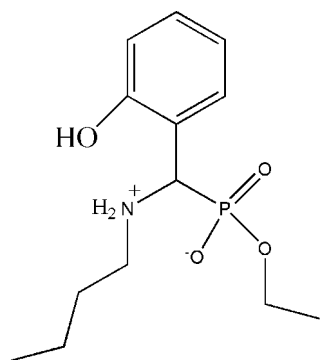Correspondence e-mail: xdzhang@lnu.edu.cn

The title compound, $C_{13}H_{22}NO_4P$, crystallizes as a zwitterion. The crystal packing exhibits N—H···O and O—H···O hydrogen bonds, leading to the formation of a three-dimensional supramolecular network. Three C atoms, one in the *n*Bu group and two in the Et group, are disordered over two positions; the site occupancy factors are *ca.* 0.8/0.2, 0.7/0.3 and 0.6/0.4.

Related literature

For related literature, see: Kurzak *et al.* (2000); Sawka-Dobrowolska (1985); Xu & Fu (2001); Xu *et al.* (2000); Zhang *et al.* (2005).

Experimental

Crystal data

$C_{13}H_{22}NO_4P$	$Z = 16$
$M_r = 287.29$	Mo $K\alpha$ radiation
Tetragonal, $I4_1/a$	$\mu = 0.17$ mm^{-1}
$a = 21.896$ (3) Å	$T = 293$ (2) K
$c = 14.059$ (2) Å	$0.31 \times 0.25 \times 0.20$ mm
$V = 6740.4$ (16) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	3807 measured reflections
	2986 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	1911 reflections with $I > 2\sigma(I)$
$T_{min} = 0.950$, $T_{max} = 0.967$	$R_{int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.070$	42 restraints
$wR(F^2) = 0.243$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{max} = 0.54$ e Å^{-3}
2986 reflections	$\Delta\rho_{min} = -0.50$ e Å^{-3}
184 parameters	

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O1[i]	0.82	1.90	2.651 (4)	153
N1—H1B···O3[ii]	0.90	1.81	2.709 (4)	173
N1—H1A···O1[iii]	0.90	1.92	2.766 (4)	156

Symmetry codes: (i) $y + \frac{1}{4}, -x + \frac{5}{4}, z + \frac{1}{4}$; (ii) $y + \frac{1}{4}, -x + \frac{7}{4}, -z + \frac{7}{4}$; (iii) $-y + \frac{7}{4}, x - \frac{1}{4}, -z + \frac{7}{4}$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXL97*.

References

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supplementary materials

Ethyl [(*n*-butylammonio)(2-hydroxyphenyl)methyl]phosphonate

X. Zhang, C. Ge, X. Zhang and Q. Liu

Comment

The structure of the title compound,(I), is shown in Fig. 1. The interest of derivatives of aminophosphonic acids is focused on their ability to construction organic-inorganic porous supramolecular frameworks. Phosphonate derivatives have been studied by single-crystal X-ray structure analysis. For related literature, see (Kurzak *et al.*, 2000; Sawka-Dobrowolska,1985; Xu *et al.*, 2000; Xu & Fu, 2001). A three dimensional supramolecular network was formed by inter-molecular hydrogen bonds (Table 1, Fig.2).

Experimental

The target compound was synthesize according to the reported method (Zhang *et al.*, 2005). All chemicals were of reagent grade and commercially available, and were used without further purification. A mixture of salicylaldehyde (0.02 mol) and butylamine (1.97 ml) in ethanol (30 ml) was refluxed for 10 h. An ethanol solution (20 ml) of diethyl phosphonate (0.02 mol) was then added drop wise. The resulting solution was refluxed until a solid appeared. The solid product was filtered off, washed with ethanol and recrystallized from water to give (I) in 63% yield.

Refinement

Atom C11 of the *n*-butyl group and atoms C12 and C13 of the ethyl group are disordered over two sites: occupancies 0.80/0.20, 0.70/0.30 and 0.62/0.38, respectively. H-atoms were not included for the lesser occupied atoms. H atoms attached to the C atoms were placed in geometrically idealized positions and treated as riding atoms; C—H = 0.93–0.98 Å with $U_{iso}(H)=1.2U_{eq}$. The O—H and N—H hydrogen atoms were placed in calculated positons and treated as riding atoms: Distances O—H = 0.82 Å, with $U_{iso}(H) = 1.5U_{eq}(O)$, and N—H = 0.90 Å with $U_{iso}(H) = 1.2U_{eq}(N)$.
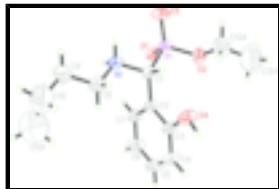
Figures

Fig. 1. The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level(arbitrary sphere for the H atoms).
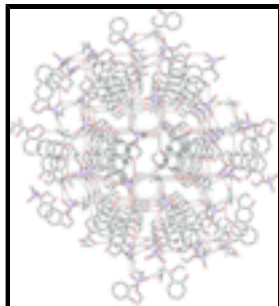
supplementary materials

Fig. 2. Two-dimensional structure of (I) formed by hydrogen bonds (viewed along 001 direction).

Ethyl [(n-butylammonio)(2-hydroxyphenyl)methyl]phosphonate

Crystal data

$C_{13}H_{22}NO_4P$	$Z = 16$
$M_r = 287.29$	$F_{000} = 2464$
Tetragonal, $I4_1/a$	$D_x = 1.132$ Mg m^{-3}
Hall symbol: -I4ad	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 21.896$ (3) Å	Cell parameters from 744 reflections
$b = 21.896$ (3) Å	$\theta = 2.9$–$22.5°$
$c = 14.059$ (2) Å	$\mu = 0.17$ mm^{-1}
$\alpha = 90°$	$T = 293$ (2) K
$\beta = 90°$	Block, yellow
$\gamma = 90°$	$0.31 \times 0.25 \times 0.20$ mm
$V = 6740.4$ (16) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	2986 independent reflections
Radiation source: fine-focus sealed tube	1911 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.027$
$T = 293(2)$ K	$\theta_{max} = 25.0°$
phi and ω scans	$\theta_{min} = 1.7°$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$h = -26 \rightarrow 1$
$T_{min} = 0.950$, $T_{max} = 0.967$	$k = -1 \rightarrow 26$
3807 measured reflections	$l = -16 \rightarrow 1$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.070$	$w = 1/[\sigma^2(F_o^2) + (0.157P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.243$	$(\Delta/\sigma)_{max} = 0.001$

$S = 1.04$		$\Delta\rho_{max} = 0.54$ e Å^{-3}
2986 reflections		$\Delta\rho_{min} = -0.50$ e Å^{-3}
184 parameters		Extinction correction: none
42 restraints		
Primary atom site location: structure-invariant direct methods		
Secondary atom site location: difference Fourier map		

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
P1	0.94165 (4)	0.62363 (4)	0.79003 (8)	0.0553 (4)	
O1	0.89072 (11)	0.66681 (11)	0.7711 (2)	0.0615 (7)	
O2	0.92802 (14)	0.56485 (13)	0.7277 (2)	0.0783 (9)	
O3	1.00450 (12)	0.64563 (14)	0.7782 (2)	0.0750 (9)	
O4	0.91293 (13)	0.46901 (12)	0.9416 (3)	0.0818 (10)	
H4	0.9035	0.4340	0.9560	0.123*	
N1	0.95690 (13)	0.63817 (13)	0.9811 (2)	0.0552 (8)	
H1A	0.9960	0.6475	0.9679	0.066*	
H1B	0.9347	0.6725	0.9745	0.066*	
C1	0.93477 (15)	0.59188 (16)	0.9100 (3)	0.0531 (9)	
H1	0.9626	0.5569	0.9135	0.064*	
C2	0.87154 (16)	0.56846 (16)	0.9342 (3)	0.0537 (9)	
C3	0.86297 (17)	0.50615 (17)	0.9501 (3)	0.0589 (10)	
C4	0.80561 (18)	0.48414 (19)	0.9738 (3)	0.0715 (12)	
H4A	0.7998	0.4425	0.9835	0.086*	
C5	0.75756 (19)	0.5236 (2)	0.9828 (4)	0.0782 (13)	
H5	0.7191	0.5086	0.9987	0.094*	
C6	0.76562 (18)	0.5856 (2)	0.9686 (3)	0.0782 (13)	
H6	0.7330	0.6123	0.9759	0.094*	
C7	0.82280 (17)	0.60747 (18)	0.9434 (3)	0.0672 (12)	
H7	0.8282	0.6490	0.9326	0.081*	
C8	0.9529 (2)	0.61727 (19)	1.0824 (3)	0.0695 (11)	
H8A	0.9109	0.6070	1.0973	0.083*	
H8B	0.9775	0.5808	1.0906	0.083*	
C9	0.9745 (3)	0.6652 (3)	1.1483 (4)	0.0982 (16)	

H9A	0.9524	0.7028	1.1362	0.118*	
H9B	1.0175	0.6729	1.1373	0.118*	
C10	0.9650 (3)	0.6461 (3)	1.2496 (5)	0.194 (4)	
H10A	0.9914	0.6695	1.2914	0.232*	
H10B	0.9744	0.6031	1.2573	0.232*	
C11A	0.8971 (3)	0.6584 (3)	1.2739 (5)	0.290 (9)	0.80
H11A	0.8834	0.6943	1.2408	0.436*	
H11B	0.8928	0.6645	1.3412	0.436*	
H11C	0.8728	0.6240	1.2546	0.436*	
C11B	0.9637 (3)	0.6963 (3)	1.3273 (5)	0.32 (4)	0.20
C12A	0.9683 (3)	0.5207 (3)	0.7069 (5)	0.120 (3)	0.70
H12A	0.9780	0.4968	0.7630	0.144*	
H12B	1.0057	0.5379	0.6815	0.144*	
C12B	0.9414 (3)	0.5597 (3)	0.6272 (5)	0.143 (8)	0.30
C13A	0.9357 (3)	0.4809 (3)	0.6314 (5)	0.238 (8)	0.62
H13A	0.8933	0.4769	0.6477	0.356*	
H13B	0.9543	0.4412	0.6294	0.356*	
H13C	0.9392	0.5000	0.5701	0.356*	
C13B	0.9999 (3)	0.5229 (3)	0.6033 (5)	0.242 (14)	0.38

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0424 (6)	0.0494 (6)	0.0739 (7)	−0.0022 (4)	−0.0018 (4)	0.0012 (5)
O1	0.0482 (14)	0.0513 (15)	0.0850 (19)	0.0009 (11)	−0.0106 (13)	0.0039 (13)
O2	0.079 (2)	0.0618 (17)	0.094 (2)	0.0035 (15)	0.0061 (16)	−0.0180 (16)
O3	0.0428 (15)	0.094 (2)	0.088 (2)	−0.0119 (14)	0.0022 (14)	0.0175 (17)
O4	0.0612 (17)	0.0484 (16)	0.136 (3)	0.0045 (14)	0.0095 (17)	0.0238 (17)
N1	0.0455 (16)	0.0468 (16)	0.073 (2)	0.0004 (13)	−0.0009 (14)	0.0085 (15)
C1	0.0408 (18)	0.0426 (18)	0.076 (3)	0.0029 (14)	0.0007 (17)	0.0009 (17)
C2	0.0438 (19)	0.048 (2)	0.069 (2)	−0.0010 (15)	0.0018 (17)	0.0040 (17)
C3	0.048 (2)	0.047 (2)	0.082 (3)	−0.0004 (16)	−0.0022 (18)	0.0127 (19)
C4	0.055 (2)	0.058 (2)	0.101 (3)	−0.0114 (19)	−0.005 (2)	0.022 (2)
C5	0.045 (2)	0.089 (3)	0.100 (3)	−0.016 (2)	0.003 (2)	0.019 (3)
C6	0.045 (2)	0.080 (3)	0.110 (4)	0.008 (2)	0.007 (2)	0.008 (3)
C7	0.048 (2)	0.053 (2)	0.101 (3)	0.0011 (17)	0.004 (2)	0.007 (2)
C8	0.070 (3)	0.064 (2)	0.075 (3)	−0.006 (2)	0.002 (2)	0.009 (2)
C9	0.106 (4)	0.112 (4)	0.076 (3)	−0.011 (3)	−0.010 (3)	−0.005 (3)
C10	0.230 (8)	0.185 (7)	0.167 (6)	−0.008 (7)	−0.023 (6)	−0.032 (6)
C11A	0.309 (12)	0.283 (12)	0.279 (12)	−0.008 (9)	0.025 (9)	−0.036 (9)
C11B	0.32 (4)	0.32 (4)	0.32 (4)	−0.002 (10)	−0.001 (10)	−0.007 (10)
C12A	0.116 (6)	0.104 (5)	0.140 (6)	0.022 (5)	0.007 (5)	−0.020 (5)
C12B	0.153 (12)	0.135 (11)	0.143 (11)	−0.011 (9)	0.015 (9)	−0.008 (9)
C13A	0.249 (12)	0.222 (11)	0.241 (11)	0.016 (9)	0.006 (9)	−0.064 (9)
C13B	0.247 (16)	0.248 (17)	0.231 (16)	0.004 (10)	−0.003 (10)	0.001 (10)

Geometric parameters (Å, °)

P1—O3	1.468 (3)	C6—H6	0.9300

P1—O1	1.486 (3)	C7—H7	0.9300
P1—O2	1.586 (3)	C8—C9	1.478 (7)
P1—C1	1.830 (4)	C8—H8A	0.9700
O2—C12A	1.340 (6)	C8—H8B	0.9700
O2—C12B	1.448 (7)	C9—C10	1.499 (8)
O4—C3	1.368 (4)	C9—H9A	0.9700
O4—H4	0.8200	C9—H9B	0.9700
N1—C8	1.498 (5)	C10—C11A	1.5499
N1—C1	1.504 (5)	C10—H10A	0.9700
N1—H1A	0.9000	C10—H10B	0.9700
N1—H1B	0.9000	C11A—H11A	0.9600
C1—C2	1.515 (5)	C11A—H11B	0.9600
C1—H1	0.9800	C11A—H11C	0.9600
C2—C7	1.373 (5)	C12A—C13A	1.5481
C2—C3	1.395 (5)	C12A—H12A	0.9700
C3—C4	1.386 (5)	C12A—H12B	0.9700
C4—C5	1.367 (6)	C12B—C13B	1.5498
C4—H4A	0.9300	C13A—H13A	0.9600
C5—C6	1.383 (6)	C13A—H13B	0.9600
C5—H5	0.9300	C13A—H13C	0.9600
C6—C7	1.387 (5)		
O3—P1—O1	118.33 (17)	C6—C7—H7	119.6
O3—P1—O2	112.34 (18)	C9—C8—N1	111.1 (4)
O1—P1—O2	106.03 (17)	C9—C8—H8A	109.4
O3—P1—C1	107.84 (16)	N1—C8—H8A	109.4
O1—P1—C1	110.18 (16)	C9—C8—H8B	109.4
O2—P1—C1	100.70 (17)	N1—C8—H8B	109.4
C12A—O2—C12B	66.3 (3)	H8A—C8—H8B	108.0
C12A—O2—P1	125.6 (4)	C8—C9—C10	110.7 (5)
C12B—O2—P1	124.4 (3)	C8—C9—H9A	109.5
C3—O4—H4	109.5	C10—C9—H9A	109.5
C8—N1—C1	114.0 (3)	C8—C9—H9B	109.5
C8—N1—H1A	108.7	C10—C9—H9B	109.5
C1—N1—H1A	108.7	H9A—C9—H9B	108.1
C8—N1—H1B	108.7	C9—C10—C11A	107.1 (3)
C1—N1—H1B	108.7	C9—C10—H10A	110.3
H1A—N1—H1B	107.6	C11A—C10—H10A	110.3
N1—C1—C2	111.9 (3)	C9—C10—H10B	110.3
N1—C1—P1	109.3 (2)	C11A—C10—H10B	110.3
C2—C1—P1	114.2 (2)	H10A—C10—H10B	108.6
N1—C1—H1	107.0	C10—C11A—H11A	109.5
C2—C1—H1	107.0	C10—C11A—H11B	109.5
P1—C1—H1	107.0	H11A—C11A—H11B	109.5
C7—C2—C3	119.2 (3)	C10—C11A—H11C	109.5
C7—C2—C1	121.4 (3)	H11A—C11A—H11C	109.5
C3—C2—C1	119.3 (3)	H11B—C11A—H11C	109.5
O4—C3—C4	122.6 (3)	O2—C12A—C13A	104.6 (3)
O4—C3—C2	117.4 (3)	O2—C12A—H12A	110.8
C4—C3—C2	120.0 (3)	C13A—C12A—H12A	110.8

C5—C4—C3	120.0 (4)	O2—C12A—H12B	110.8
C5—C4—H4A	120.0	C13A—C12A—H12B	110.8
C3—C4—H4A	120.0	H12A—C12A—H12B	108.9
C4—C5—C6	120.6 (4)	O2—C12B—C13B	114.8 (3)
C4—C5—H5	119.7	C12A—C13A—H13A	109.5
C6—C5—H5	119.7	C12A—C13A—H13B	109.5
C5—C6—C7	119.4 (4)	H13A—C13A—H13B	109.5
C5—C6—H6	120.3	C12A—C13A—H13C	109.5
C7—C6—H6	120.3	H13A—C13A—H13C	109.5
C2—C7—C6	120.7 (4)	H13B—C13A—H13C	109.5
C2—C7—H7	119.6		
O3—P1—O2—C12A	33.7 (5)	C7—C2—C3—O4	−179.0 (4)
O1—P1—O2—C12A	164.4 (4)	C1—C2—C3—O4	−0.9 (6)
C1—P1—O2—C12A	−80.8 (5)	C7—C2—C3—C4	0.9 (6)
O3—P1—O2—C12B	−50.1 (4)	C1—C2—C3—C4	179.0 (4)
O1—P1—O2—C12B	80.6 (4)	O4—C3—C4—C5	178.9 (4)
C1—P1—O2—C12B	−164.6 (4)	C2—C3—C4—C5	−1.0 (7)
C8—N1—C1—C2	52.0 (4)	C3—C4—C5—C6	0.0 (7)
C8—N1—C1—P1	179.5 (3)	C4—C5—C6—C7	1.1 (8)
O3—P1—C1—N1	52.3 (3)	C3—C2—C7—C6	0.2 (6)
O1—P1—C1—N1	−78.2 (2)	C1—C2—C7—C6	−177.9 (4)
O2—P1—C1—N1	170.2 (2)	C5—C6—C7—C2	−1.2 (7)
O3—P1—C1—C2	178.6 (3)	C1—N1—C8—C9	−179.2 (4)
O1—P1—C1—C2	48.1 (3)	N1—C8—C9—C10	174.9 (4)
O2—P1—C1—C2	−63.6 (3)	C8—C9—C10—C11A	−80.4 (4)
N1—C1—C2—C7	57.4 (5)	C12B—O2—C12A—C13A	−54.1 (2)
P1—C1—C2—C7	−67.4 (4)	P1—O2—C12A—C13A	−170.5 (2)
N1—C1—C2—C3	−120.7 (4)	C12A—O2—C12B—C13B	−16.6 (3)
P1—C1—C2—C3	114.5 (3)	P1—O2—C12B—C13B	101.4 (3)

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O1[i]	0.82	1.90	2.651 (4)	153
N1—H1B···O3[ii]	0.90	1.81	2.709 (4)	173
N1—H1A···O1[iii]	0.90	1.92	2.766 (4)	156

Symmetry codes: (i) $y+1/4$, $-x+5/4$, $z+1/4$; (ii) $y+1/4$, $-x+7/4$, $-z+7/4$; (iii) $-y+7/4$, $x-1/4$, $-z+7/4$.
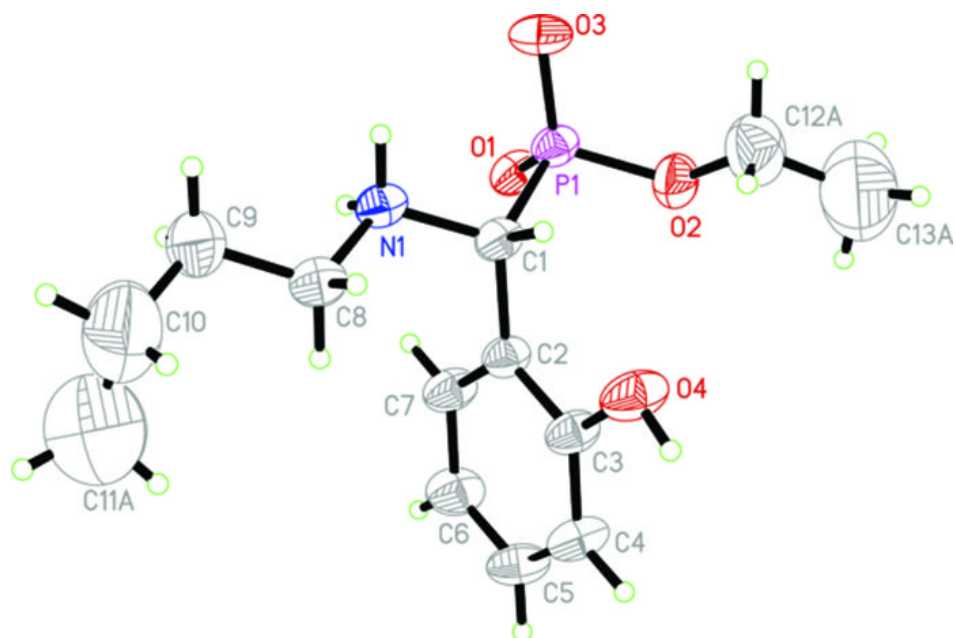
Fig. 1

Fig. 2