$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O2—C12	1.222 (4)	C15—C20	1.516 (4)
O3—C18	1.212 (4)	C15—C16	1.555 (4)
C9—C12	1.496 (4)	C16—C18	1.510 (5)
C12—C13	1.518 (5)	C18—C19	1.467 (5)
C13—C15	1.548 (4)	C19—C20	1.366 (4)
O2—C12—C9	118.4 (3)	C13—C15—C16	113.9 (3)
O2—C12—C13	119.3 (3)	C18—C16—C15	105.0 (3)
C9—C12—C13	122.3 (3)	O3—C18—C19	126.1 (4)
C12—C13—C14	110.0 (3)	O3—C18—C16	126.0 (3)
C12—C13—C15	112.2 (3)	C19—C18—C16	107.8 (3)
C14—C13—C15	110.7 (3)	C20—C19—C18	109.9 (3)
C20—C15—C13	111.9 (2)	C19—C20—C15	111.7 (3)
C20—C15—C16	102.9 (3)		

Intensities above 24° in θ were very weak and not measured.

Data collection: *XSCANS* (Siemens, 1993). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1195). Services for accessing these data are described at the back of the journal.

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Four *N*-Benzyl-Substituted 2-Ethyl-3-hydroxypyridin-4-ones

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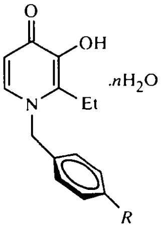
Abstract

The molecular structures of 1-benzyl-2-ethyl-3-hydroxypyridin-4-one hydrate [(1), $C_{14}H_{15}NO_2.H_2O$], 2-ethyl-3-hydroxy-1-(4-methylbenzyl)pyridin-4-one [(2), $C_{15}H_{17}NO_2$], 2-ethyl-1-(4-fluorobenzyl)-3-hydroxypyridin-4-one [(3), $C_{14}H_{14}FNO_2$] and 2-ethyl-3-hydroxy-1-(4-trifluoromethylbenzyl)pyridin-4-one hemihydrate [(4), $C_{15}H_{14}F_3NO_2.0.5H_2O$] have been determined. The compounds all exhibit mutually hydrogen-bonded dimeric pairs. In the case of (1) and (2), the molecules of the dimer are symmetry related, while in (3) and (4), two independent molecules of the asymmetric unit are linked. For the hydrates (1) and (4), the dimeric pairs are linked by further hydrogen bonds through the water molecules.

Comment

The title structures form dimeric units through mutual O1—H1···O2 hydrogen bonds (Figs. 1, 2, 3 and 4). This type of dimeric structure is commonly found for the anhydrous 3-hydroxypyridin-4-ones (Hider *et al.*, 1990; Chan *et al.*, 1992; Xiao *et al.*, 1992; Burgess *et al.*, 1993, 1998) and 3-hydroxypyran-4-ones, which have also been reported as hydrogen-bonded chains (Burgess *et al.*, 1996; Brown *et al.*, 1995). Important bond distances in compounds (1), (2), (3) and (4) are essentially the same within experimental error.



(1) R = H; n = 1
(2) R = Me; n = 0
(3) R = F; n = 0
(4) R = CF$_3$; n = 0.5

In the case of (1) and (2), the dimeric pair is related by a centre of symmetry at 0,0,0 and $\frac{1}{2},\frac{1}{2},0$, respectively,

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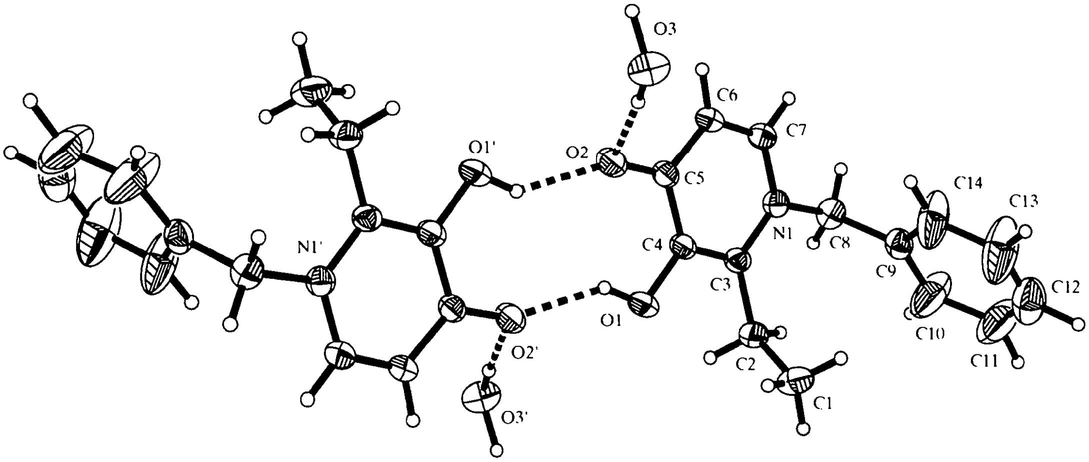

Fig. 1. The molecular structure of dimer (1) showing the atom-numbering scheme and 30% displacement ellipsoids. Primed atoms are generated by a centre of symmetry [symmetry code: (′) −*x*, −*y*, −*z*]. Intermolecular O—H···O bonds are shown as dashed lines. H atoms are drawn as spheres of arbitrary radii.

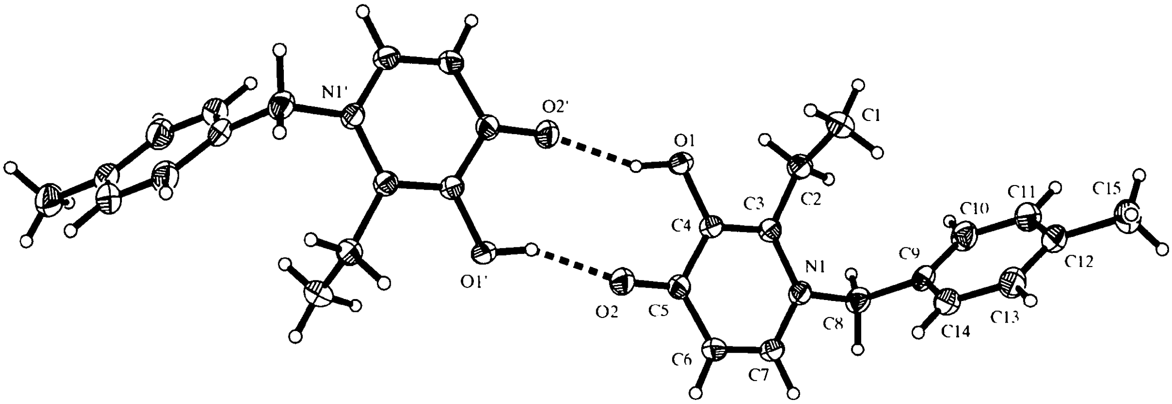

Fig. 2. The molecular structure of (2) showing the atom-numbering scheme and 30% displacement ellipsoids. Primed atoms are generated by a centre of symmetry [symmetry code: (′) 1 − *x*, 1 − *y*, −*z*]. Intermolecular hydrogen bonds are shown as dashed lines.

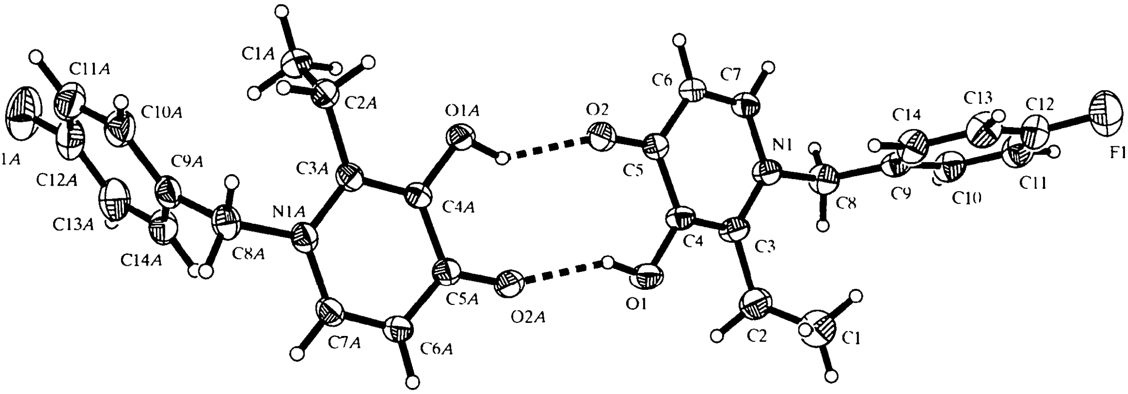

Fig. 3. The molecular structure of (3) showing the atom-numbering scheme and 30% displacement ellipsoids. Intermolecular hydrogen bonds are shown as dashed lines.

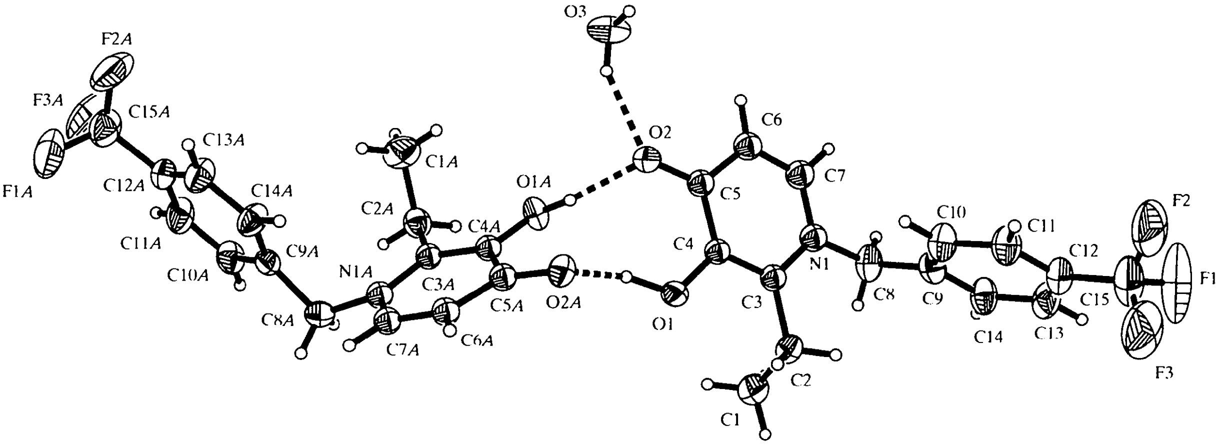

Fig. 4. The molecular structure of (4) showing the atom-numbering scheme and 30% displacement ellipsoids. Intermolecular hydrogen bonds are shown as dashed lines.

and, therefore, both structures have two equivalent O1—H1···O2 hydrogen bonds where the O···O distance is 2.700 (4) for (1) and 2.692 (1) Å for (2). For both (3) and (4), two independent molecules of the asymmetric unit are linked with O···O distances of 2.699 (2) and 2.639 (2) Å, and 2.582 (3) and 2.640 (4) Å, respectively. The stuctures of the hydrates (1) and (4) show that the hydrogen-bonded dimeric pairs are further linked by hydrogen-bond bridges through the water molecules. For (1), there is one water molecule associated with each pyridinone molecule, and symmetry-related water molecules link adjacent dimers with double hydrate bridges (Fig. 1). The hydrogen bonds link O2 atoms of adjacent dimers with symmetric O2···O3 distances of 2.925 (4) and 2.949 (4) Å. For (4), one water molecule is associated with the two unique pyridinone molecules of the dimeric pair, linking the O2 atom of one dimer with the O1*A* atom of an adjacent dimeric pair with a single asymmetric hydrogen-bonded water bridge [O2···O3 2.756 (4) and O3···O1$A^{\rm iii}$ 3.143 (4) Å; symmetry code: (iii) $\frac{3}{2}-x, y+\frac{1}{2}, 2-z$]. For all four stuctures, the dimers are further linked by weak C—H···O hydrogen bonds of the order C···O 3.3 Å, as previously observed for this type of compound (Burgess *et al.*, 1996, 1998).

Experimental

Compounds (1), (2), (3) and (4) were prepared by the reaction of ethyl maltol (4.2 g, 30 mmol) with the appropriate benzylamine (60 mmol) in dilute HCl (50 ml) with reflux for 72 h and hot filtration. Crystals suitable for X-ray analyses were obtained from hot methanol.

Compound (1)

Crystal data

$C_{14}H_{15}NO_2.H_2O$
$M_r = 247.29$
Triclinic
$P\bar{1}$
$a = 7.382\,(1)$ Å
$b = 7.791\,(1)$ Å
$c = 11.437\,(1)$ Å
$\alpha = 94.11\,(1)^\circ$
$\beta = 101.70\,(1)^\circ$
$\gamma = 93.39\,(1)^\circ$
$V = 640.62\,(13)$ Å^3
$Z = 2$
$D_x = 1.282$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 4.4$–11.9°
$\mu = 0.090$ mm^{-1}
$T = 293\,(2)$ K
Block
0.59 × 0.23 × 0.21 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
2824 measured reflections
2253 independent reflections
1540 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$

$\theta_{\rm max} = 25^\circ$
$h = -1 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -13 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.076$
$wR(F^2) = 0.228$
$S = 1.055$
2252 reflections
161 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0869P)^2 + 0.7922P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.418$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.327$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (2)

Crystal data

$C_{15}H_{17}NO_2$
$M_r = 243.30$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Triclinic
$P\bar{1}$
$a = 7.2766\ (7)$ Å
$b = 7.3473\ (6)$ Å
$c = 13.294\ (1)$ Å
$\alpha = 91.395\ (6)°$
$\beta = 90.823\ (8)°$
$\gamma = 117.258\ (9)°$
$V = 631.37\ (9)$ Å^3
$Z = 2$
$D_x = 1.280$ Mg m^{-3}
D_m not measured

Cell parameters from 27 reflections
$\theta = 5.46–12.40°$
$\mu = 0.085$ mm^{-1}
$T = 190\ (2)$ K
Block
0.58 × 0.48 × 0.23 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
2605 measured reflections
2222 independent reflections
1980 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$

$\theta_{\rm max} = 25°$
$h = -7 \rightarrow 8$
$k = -8 \rightarrow 1$
$l = -15 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.114$
$S = 1.031$
2222 reflections
165 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 0.2944P]$ where $P = F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.005$
$\Delta\rho_{\rm max} = 0.306$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.267$ e Å^{-3}
Extinction correction: *SHELXTL/PC*
Extinction coefficient: 0.066 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (3)

Crystal data

$C_{14}H_{14}FNO_2$
$M_r = 247.26$
Triclinic
$P\bar{1}$
$a = 7.266\ (1)$ Å
$b = 12.408\ (2)$ Å
$c = 14.681\ (2)$ Å
$\alpha = 113.05\ (1)°$
$\beta = 100.20\ (1)°$
$\gamma = 90.74\ (1)°$
$V = 1193.7\ (3)$ Å^3
$Z = 4$
$D_x = 1.376$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 27 reflections
$\theta = 2.61–12.49°$
$\mu = 0.102$ mm^{-1}
$T = 190\ (2)$ K
Plate
0.49 × 0.34 × 0.15 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
4713 measured reflections
4013 independent reflections
3167 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.012$

$\theta_{\rm max} = 25°$
$h = -1 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -17 \rightarrow 17$
3 standard reflections every 100 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.099$
$S = 1.043$
4013 reflections
333 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0473P)^2 + 0.3277P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.008$
$\Delta\rho_{\rm max} = 0.231$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.184$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (4)

Crystal data

$C_{15}H_{14}F_3NO_2.0.5H_2O$
$M_r = 306.28$
Monoclinic
$P2_1/a$
$a = 14.645\ (1)$ Å
$b = 11.634\ (1)$ Å
$c = 17.832\ (3)$ Å
$\beta = 110.10\ (2)°$
$V = 2853.2\ (6)$ Å^3
$Z = 8$
$D_x = 1.426$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 38 reflections
$\theta = 5.19–12.45°$
$\mu = 0.123$ mm^{-1}
$T = 190\ (2)$ K
Plate
0.66 × 0.62 × 0.10 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: semi-empirical based on ψ-scan data (*XEMP* in *SHELXTL/PC*; Sheldrick, 1996)
$T_{\rm min} = 0.906$, $T_{\rm max} = 0.995$
5398 measured reflections
4950 independent reflections

2912 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\rm max} = 25°$
$h = -1 \rightarrow 16$
$k = -1 \rightarrow 13$
$l = -21 \rightarrow 19$
3 standard reflections every 97 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.165$
$S = 1.023$
4949 reflections
328 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2 + 4.2315P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.001$
$\Delta\rho_{\rm max} = 0.448$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.306$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond distances (Å) for compounds (1), (2), (3) and (4)*

	(1)	(2)	(3)†	(4)†
O1—C4	1.357 (4)	1.363 (2)	1.363 (2)	1.353 (4)
O1*A*—C4*A*			1.357 (2)	1.372 (4)
O2—C5	1.279 (4)	1.265 (2)	1.266 (2)	1.280 (4)
O2*A*—C5*A*			1.267 (2)	1.266 (4)

N1—C8	1.478 (4)	1.481 (2)	1.474 (2)	1.475 (5)
N1*A*—C8*A*			1.477 (2)	1.476 (5)
C3—C4	1.370 (5)	1.371 (2)	1.370 (2)	1.373 (5)
C3*A*—C4*A*			1.371 (2)	1.367 (5)
C4—C5	1.420 (5)	1.439 (2)	1.435 (2)	1.433 (5)
C4*A*—C5*A*			1.438 (2)	1.437 (5)

† Two independent molecules.

Table 2. *Hydrogen-bonding geometry (Å, °) for compounds (1), (2), (3) and (4)*

Compound	*D*—H···*A*	*D*···*A*	H···*A*	*D*—H···*A*
(1)	O1—H1···O2^{i}	2.700 (4)	1.919	142.4
(2)	O1—H1···O2^{ii}	2.692 (1)	1.802	145.7
(3)	O1—H1···O2*A*	2.699 (2)	1.919	150.7
	O1*A*—H1*A*···O2	2.639 (2)	1.815	154.2
(4)	O1—H1···O2*A*	2.582 (3)	1.468	167.3
	O1*A*—H1*A*···O2	2.640 (4)	1.744	145.2

Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, 1-y, -z$.

For all four structures, the bridging H atoms were located as the highest residual electron density when all other atoms were included in the refinement. For the final refinement cycles, the positional parameters of the bridging H atoms and those of the calculated C—H atoms were constrained using a riding model.

For all compounds, data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1996); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1028). Services for accessing these data are described at the back of the journal.

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Tris{[tris(2-hydroxymethyl)methyl]ammonium} D-3-Phosphoglycerate at 150 K and Tris(cyclohexylammonium) D-3-Phosphoglycerate Ethanol Solvate at 85 K

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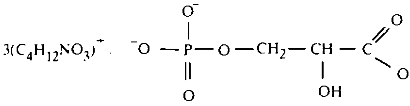
Abstract

The structures of the D-3-phosphoglycerate trianion in the tris{[tris(2-hydroxymethyl)methyl]ammonium} salt, $3C_4H_{12}NO_3^+.C_3H_4O_7P^{3-}$, (I), and in the tris(cyclohexylammonium) ethanol solvate, $3C_6H_{14}N^+.C_3H_4O_7P^{3-}.C_2H_5OH$, (II), have been determined by X-ray analyses at 150 and 85 K, respectively. A notable feature of (I) is the shortest P—O(ester) bond [1.607 (2) Å] found so far for the completely ionized phosphate ester group. In contrast, in (II), this bond length is 1.627 (2) Å, similar to that observed in doubly ionized phosphate ester groups. In (II), the carboxylate group is twisted by −23.5 (4)° relative to the α-hydroxyl group, as indicated by the O1—C1—C2—O2 torsion angle, whereas in (I), the O2—C2—C1—O1 system is almost planar. Both crystal structures are stabilized by hydrogen bonds utilizing all N and O atoms.

Comment

The investigation presented in this paper is part of our systematic studies of D-3-phosphoglycerates (3-PGA) with different ionization states (Jerzykiewicz & Lis, 1997). In previous papers, the structures of mono-ionized (Lis & Jerzykiewicz, 1995) and doubly ionized 3-PGA anions (Lis & Jerzykiewicz, 1996; Jerzykiewicz & Lis, 1997) were reported. We now describe the crystal structures of the completely ionized 3-PGA anion in the tris{[tris(2-hydroxymethyl)methyl]ammonium} salt, (I), and in the tris(cyclohexylammonium) ethanol solvate, (II).



(I)

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