Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Ethane-1,1,2-trisphosphonic acid hemihydrate

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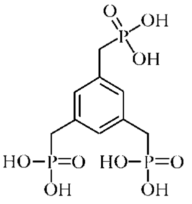
Received 15 October 2007
Accepted 28 November 2007
Online 12 January 2008

Ethane-1,1,2-trisphosphonic acid crystallizes as a hemihydrate, $C_2H_9O_9P_3 \cdot 0.5H_2O$, in which the water O atom lies on an inversion centre in the space group $P2_1/c$. The acid component, which contains a short but noncentred O—H···O hydrogen bond, adopts a *gauche* conformation. The acid components are linked by an extensive series of O—H···O hydrogen bonds to form layers, which are linked into pairs by the water molecules.

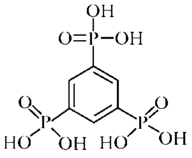
Comment

The elaboration of new materials based on the supramolecular assembly of organic molecules constitutes a dynamic field of research (Desiraju, 1995). Potential applications of such materials are diverse and include, as examples, materials for optics (Muthuraman *et al.*, 1999) or for analytical purposes (Morin *et al.*, 2005; Russell *et al.*, 1997). Moreover, knowledge of supramolecular interactions can give crucial information to the understanding of chemical transformations taking place in biochemical systems. Our first results in this area concern the study of the auto-assembly of mesitylene trisphosphonic acid (*A*), which forms dimers in the solid state (Jaffrès *et al.*, 2002) characterized by the three methylenephosphonic groups localized on the same side of the benzene ring. A second study has reported the cocrystallization of *A* with guanidinium chloride (Sopkova-de Oliveira Santos *et al.*, 2004). More recently, we have reported the crystal structure of benzenetrisphosphonic acid (*B*), which was characterized by a packing involving both strong hydrogen bonds and π stacking (Hix *et al.*, 2007). These three studies show the potential of the phosphonic acid group for building supramolecular networks.

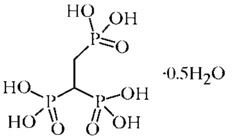
In order to study further the self-assembly of polyphosphonic derivatives, we have synthesized ethane-1,1,2-trisphosphonic acid (ETP) from hexaethyl ethylidene-1,1,2-tris(phosphonate), previously prepared following a method published recently (Delain-Bioton *et al.*, 2005). ETP has a great potential to form supramolecular networks in view of the number of hydrogen-bond donor and acceptor sites. It is of note that ETP has been identified to be, among two other polyphosphonic compounds, highly effective in its covalent grafting on titanium oxide and in inducing calcium phosphate growth on its surface (Viornery *et al.*, 2002). Therefore, this molecule has a double interest: (i) it has a great potential to form supramolecular interactions by auto-assembly and (ii) is a good candidate for coating inorganic supports.



A



B



(I)

Crystals of the title compound, (I), suitable for diffraction were obtained after leaving ETP (initially a very viscous oil) for several weeks at room temperature. The asymmetric unit contains one molecule of ETP and one-half of a water molecule (Fig. 1). The water molecule is in a special position on an inversion centre in the crystal structure, and the H atoms on the water molecule were difficult to locate from difference-density maps. The structure solution obtained from the refinement has two H atoms placed on the water atom O40 (the occupancy factor for each H atom being 0.50), two further H atoms with occupancies of 0.50 being generated by the symmetry operation. Hence, four H atoms with occupancies of

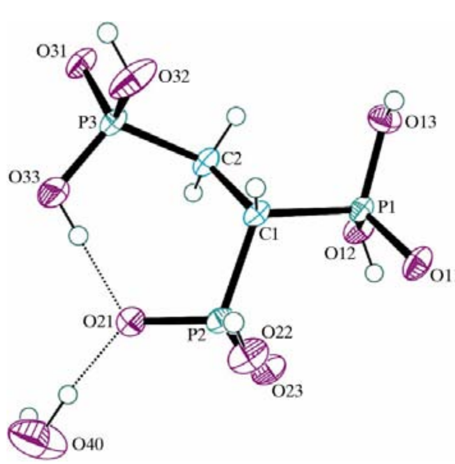


Figure 1
A displacement ellipsoid plot of the asymmetric unit of the crystal structure of (I) (with ellipsoids at the 50% probability level).

DOI: 10.1107/S0108270107064098

0.50 are present on the water O atom, illustrating the disorder associated with the exact position of the H atoms in the structure in the solid state.

The acid component adopts a *gauche* conformation in the solid state, with a P2—C1—C2—P3 torsion angle of 78.88 (11)°. One internal hydrogen bond engaging two O atoms (O21 and H33/O33 bonded to P2 and P3, respectively), is observed, in which the O21···O33 contact distance corresponds to a strong hydrogen bond.

The P=O bond lengths are about 1.49 Å, and the P—O bond lengths are between 1.5353 (14) and 1.5571 (10) Å, with the exception of the P2—O22 bond which is shorter [1.5160 (11) Å]. In the crystal structure, the P2—O22 bond is oriented face-to-face with another symmetric P2—O22 bond, and the two neighbouring O22 atoms are bound together by a hydrogen bond. The difference-density map showed two peaks in proximity to atom O22, and so two positions for atom H22 have been attributed and refined, each position having an occupancy of 0.5. The nine O atoms of phosphonic acid groups are engaged in one or two hydrogen bonds with neighbouring ETP molecules or with the water molecules, thus completing the crystal packing. Molecules of ETP are packed along the crystallographic *b* axis *via* two hydrogen bonds (O11$^{\rm v}$···H32—O32 and O31$^{\rm i}$···H12—O12; see Table 1 for symmetry codes) involving phosphonic acid groups P1 and P3 of two symmetric molecules (Fig. 2). The O···O contact distances of these hydrogen bonds correspond to the normal range for this type of hydrogen bonding between phosphonic acid groups (Jaffrès *et al.*, 2002). These chains formed along the *b*-axis direction are connected to another chain along the *c* axis (Fig. 3) *via* O23—H23···O11$^{\rm iv}$ and O13—H13···O31$^{\rm ii}$ hydrogen bonds (Table 1).

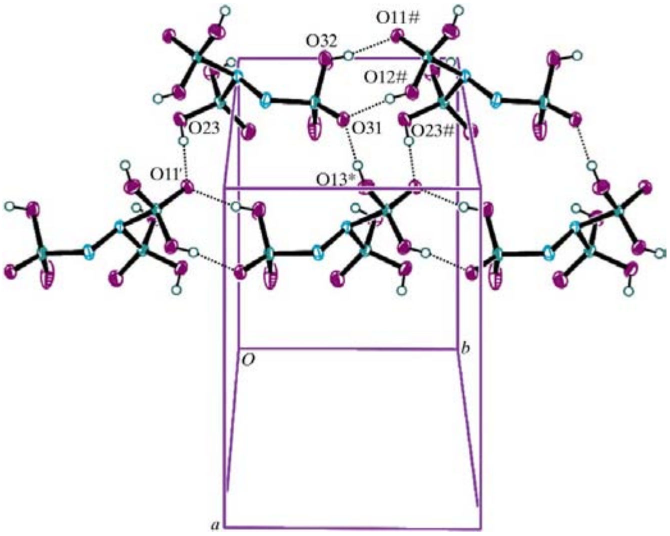


Figure 2
The packing of molecules of ETP along the *b* axis. Dashed lines indicate hydrogen bonds. [Symmetry codes: (#) $x, y + 1, z$; (*) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (′) $x, -y - \frac{1}{2}, z - \frac{1}{2}$.]

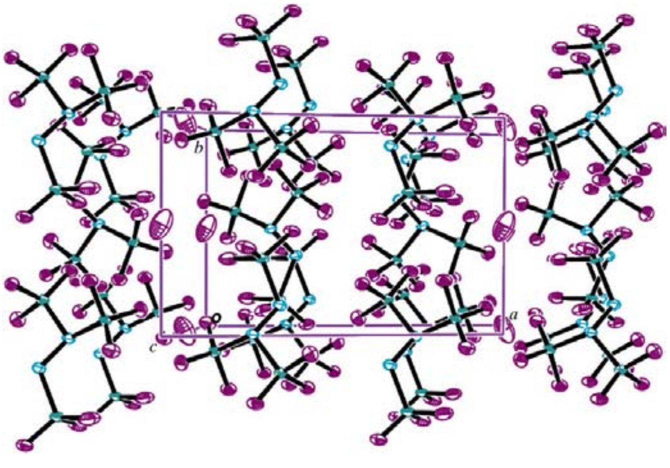


Figure 3
The packing of (I), viewed down the *c* axis.

Along the *a*-axis direction, the previously described layer in the *bc* plane is hydrogen bonded to another such layer (Fig. 3). The main bonding contribution to the cohesion of these double layers is the presence of a strong hydrogen bond occurring between the symmetrically related O22 atoms. The O22···H22—O22 distance is about 2.468 (2) Å. Additionally, there are weak hydrogen bonds involving the water molecule. Hence, the packing is best described as two-dimensional (the *a* axis is the stacking direction).

In conclusion, (I) adopts a *gauche* conformation in the solid state. The packing of this compound reveals the presence of chains running along the *b* axis involving symmetrical intermolecular O···H—O hydrogen bonds similar to those frequently observed for carboxylic acid. The chains are packed together *via* hydrogen bonds involving one molecule of water to finally define a two-dimensional structure. Furthermore, one intramolecular hydrogen bond, which certainly increases the stability of the observed *gauche* conformation, is noted. For the future, it will be interesting to study replacement of the molecule of water, which is of great importance in the packing, by other organic molecules to design new supramolecular networks.

Experimental

Hexaethyl ethylidene-1,1,2-triphosphonate (Delain-Bioton *et al.*, 2005) (2.12 g, 4.84 mmol) and concentrated HCl (60 ml, 37% in water) were heated under reflux for 16 h. The resulting solution was concentrated *in vacuo* to dryness to produce a very viscous oil (1.72 g). Propylene oxide (1 ml) was added and the resulting mixture was again concentrated *in vacuo*. High-vacuum pumping for 6 h led to the formation of a white powder (1.40 g). Dissolution in a mixture of methanol/acetone (2:1 *v*/*v*) gave a homogeneous solution. After slow evaporation at room temperature, a viscous oil was first obtained, which crystallized after five weeks. These crystals were collected by filtration and washed with methanol (yield 1.15 g, 88%). ^{1}H NMR (D$_2$O): δ 2.05 (*m*, 2H, CH$_2$P), 2.35 (*m*, 1H, PCCHP$_2$); ^{31}P NMR (D$_2$O): δ 21.2 (*d*, $^{3}J_{\rm PP}$ = 27 Hz, PCHP), 27.1 (*t*, $^{3}J_{\rm PP}$ = 27 Hz, PCH$_2$); ^{13}C NMR (D$_2$O): δ 22.8 (*dt*, $^{2}J_{\rm CP}$ = 130 Hz, $^{3}J_{\rm CP}$ < 1 Hz, PCH$_2$), 32.8 (*dt*, $^{2}J_{\rm CP}$ = 133 Hz, $^{3}J_{\rm CP}$ = 4 Hz, PCH$_2$).

Crystal data

$C_2H_9O_9P_3\cdot0.5H_2O$
$M_r = 279.01$
Monoclinic, $P2_1/c$
$a = 12.5239$ (3) Å
$b = 7.7987$ (2) Å
$c = 10.3585$ (3) Å
$\beta = 109.523$ (2)°
$V = 953.55$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.66$ mm^{-1}
$T = 273$ (2) K
0.28 × 0.16 × 0.10 mm

Data collection

Bruker Kappa-APEXII CCD area-detector diffractometer
40386 measured reflections
5036 independent reflections
3691 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.095$
$S = 1.04$
5036 reflections
163 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.58$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.60$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O12—H12···O31$^{\rm i}$	0.82	1.75	2.5584 (14)	167
O13—H13···O31$^{\rm ii}$	0.82	1.74	2.5559 (15)	177
O22—H22*B*···O22$^{\rm iii}$	0.818 (18)	1.677 (16)	2.486 (2)	169 (3)
O23—H23···O11$^{\rm iv}$	0.82	1.85	2.6632 (14)	175
O32—H32···O11$^{\rm v}$	0.82	1.81	2.6103 (15)	165
O33—H33···O21	0.82	1.65	2.4706 (16)	174
O40—H40*A*···O33$^{\rm vi}$	1.00 (2)	2.40 (3)	3.370 (2)	165 (7)
O40—H40*A*···O32$^{\rm vi}$	1.00 (2)	2.42 (7)	3.0767 (16)	123 (6)
O40—H40*B*···O21	0.99 (2)	1.92 (3)	2.8905 (11)	167 (8)

Symmetry codes: (i) $x, y-1, z$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $-x, -y, -z+2$; (iv) $x, -y-\frac{1}{2}, z-\frac{1}{2}$; (v) $x, y+1, z$; (vi) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

H atoms bonded to C atoms were refined freely, giving C—H distances in the range 0.96 (2)–1.01 (2) Å. H atoms bonded to O atoms of the acid component were treated as riding atoms, with O—H distances of 0.82 Å and $U_{\rm iso}$(H) values of 1.5$U_{\rm eq}$(O), with the exception of the H atom bonded to O22. The disorder in hydrogen occupancy on this O atom was refined using two H-atom sites, H22*A* and H22*B*, each with an occupancy of 0.5, and the correct geometry was induced using DFIX and DANG restraints (*SHELXL97*; Sheldrick, 1997*a*). A DFIX restraint was also used to refine the H atoms of water atom O40.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2006); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997*b*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

This work has been performed within the PUNCHOrga interregional network (Pôle Universitaire de Chimie Organique). We gratefully acknowledge financial support from the Ministère de la Recherche et des Nouvelles Technologies, CNRS (Centre National de la Recherche Scientifique), the Région Basse-Normandie and the European Union (FEDER funding).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3158). Services for accessing these data are described at the back of the journal.

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