Guanidinum diphenylphosphinate monohydrate

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Hydrogen bonding in the title structure, $CH_6N_3^+$·$C_{12}H_{10}O_2P^-$·H_2O or $[C(NH_2)_3]^+[Ph_2PO_2]^-$·$H_2O$, results in a bilayer architecture, which also involves π–π stacking interactions between pairs of guanidinium ions. All the cation H atoms are involved in hydrogen bonds, five to O atoms of the anion or solvent water and the sixth in an N—H$\cdots\pi$ interaction with a neighbouring phenyl ring.

Comment

Guanidinium ions have long been utilized in the modelling of Arg–Glu or Arg–Asp side-chain interactions in proteins (see, for example, Melo *et al.*, 1999; Fülscher & Mehler, 1988; Singh *et al.*, 1987). More recently, guanidinium sulfonate interactions have been utilized in supramolecular chemistry and crystal engineering. Hydrogen-bonded networks involving guanidinium salts of a range of sulfonated phosphanes and other organic sulfonates have been intensively investigated (Burrows *et al.*, 2003; Horner *et al.*, 2001; Kathó *et al.*, 2002; Smith *et al.*, 2004). In these compounds, the match between the trigonal geometry of the cation, having two hydrogen-bond donors on each edge of the triangle, and that of the sulfonate group favours the formation of infinite hydrogen-bonded arrays. These structures generally contain either bilayers or single layers, not always planar, and comprising the quasi-hexagonal GS (guanidinium sulfonate) hydrogen-bonding motif. The most important factor in determining whether a single layer or bilayer structure results appears to be the packing interactions of the organic superstructure (Horner *et al.*, 2001).

A search of the Cambridge Structural Database (Version 5.27; Allen, 2002; Fletcher *et al.*, 1996) shows no previously reported phosphinate salts of guanidinium. However, it might be expected that the mismatch between the numbers of hydrogen-bond donors and acceptors could disrupt the sheet structure observed for sulfonate analogues. We have crystallized guanidinium diphenylphosphinate as the title monohydrate, (I), which has a bilayer architecture and, perhaps surprisingly, all the hydrogen-bond donors are satisfied.
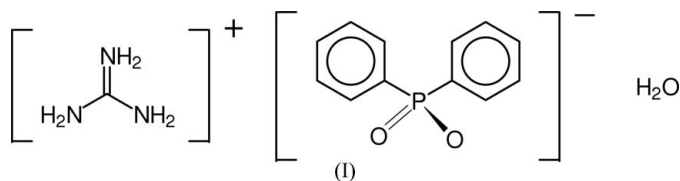

Fig. 1 shows the components of the asymmetric unit and the atom-labelling scheme for (I). The bond distances and angles
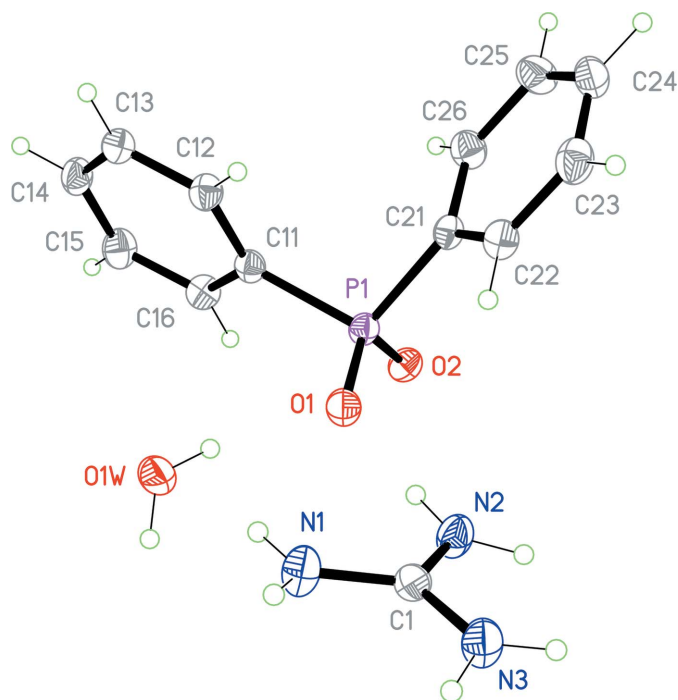
Figure 1
A perspective view of the asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level.
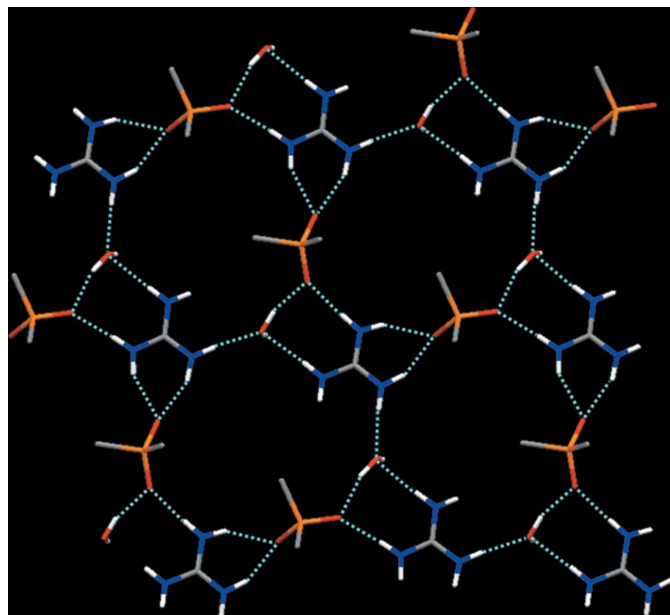

Figure 2
One layer of the hydrogen-bonded sheet, showing $R_7^7(20)$, $R_3^3(8)$ and $R_2^1(6)$ rings. Phenyl groups have been omitted for clarity. Dashed lines indicate hydrogen bonds.

Figure 3
A packing diagram, viewed along the b axis. H atoms have been omitted and the dashed lines indicate O···O and N···N non-bonded distances.

Figure 4
A perspective view of the bilayer interactions. The C1—N2^{iv} and C1^{iv}—N2 π–π interactions are shown as dashed red lines. Dashed turquoise lines indicate hydrogen bonds. [Symmetry code: (iv) $2 - x, 1 - y, 1 - z$.]

are unremarkable. Hydrogen-bond data are given in Table 1. Hydrogen bonding involving the guanidinium ion, the diphenylphosphinate O atoms and the water solvent molecule results in a hydrogen-bonded sheet (Fig. 2) lying perpendicular to the a axis, in which $R_7^7(20)$ rings (Etter *et al.*, 1990) are supported by smaller $R_3^3(8)$ and $R_2^1(6)$ patterns. All the phenyl groups of the anion lie on the same side and the sheets are paired to form a bilayer. Further hydrogen bonds link the
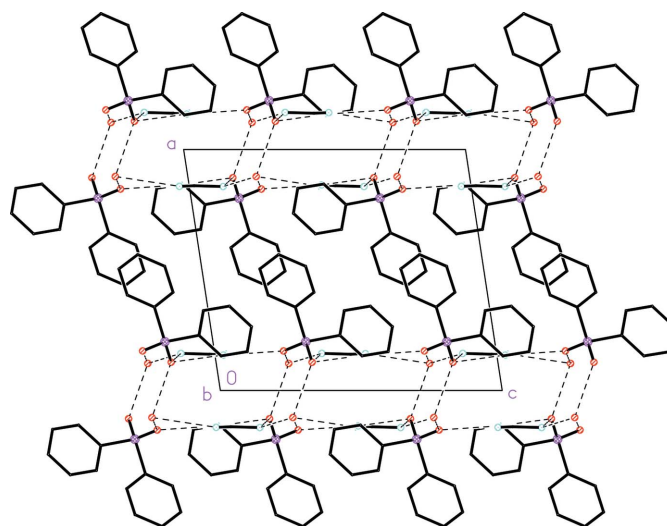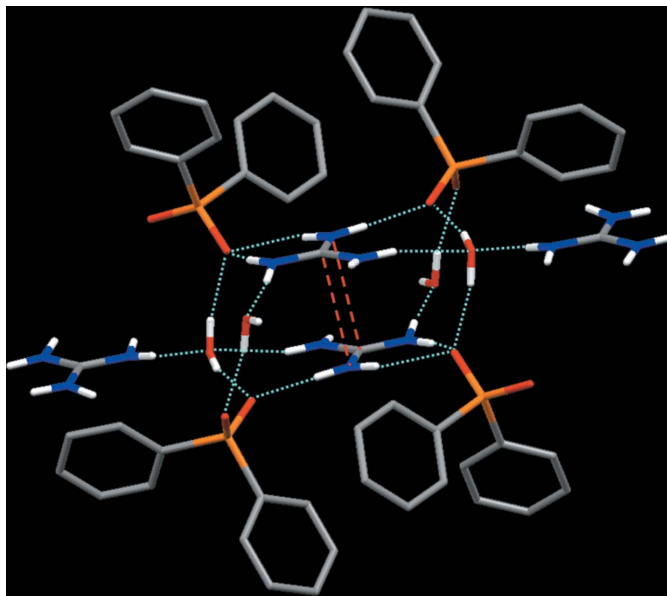
sheets together, the smallest ring being $R_5^5(12)$ (Fig. 3). In addition to the hydrogen-bonding interactions, the guanidinium ions are paired *via* π–π stacking with a symmetry-equivalent ion under operation (iv) $(2 - x, 1 - y, 1 - z)$. The interplanar distance is 3.293 (2) Å and the intermolecular C1—N2^{iv} distance is 3.332 (2) Å (Fig. 4).

Only five of the guanidinium H atoms are involved in conventional hydrogen-bonds to the diphenylphosphinate anion or water molecule (Fig. 5, Table 1). The sixth H atom (H1A) lies 2.73 (2) Å above the plane of a phenyl ring [C11–C16 under symmetry operation $(x, \frac{1}{2} - y, \frac{1}{2} + z)$]; the distance from the ring centroid to atom H1A is 2.85 (2) Å. This unusual interaction is probably responsible for the sharp signal at

Crystal data

$CH_6N_3^+ \cdot C_{12}H_{10}O_2P^- \cdot H_2O$	$D_x = 1.358$ Mg m^{-3}
$M_r = 295.27$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 5028
$a = 11.2395$ (10) Å	reflections
$b = 10.0101$ (9) Å	$\theta = 2.6–28.8°$
$c = 12.9814$ (12) Å	$\mu = 0.20$ mm^{-1}
$\beta = 98.653$ (2)°	$T = 150$ (2) K
$V = 1443.9$ (2) Å^3	Block, colourless
$Z = 4$	$0.31 \times 0.25 \times 0.21$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	2839 independent reflections
φ and ω scans	2376 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$R_{int} = 0.028$
	$\theta_{max} = 26.0°$
$T_{min} = 0.85$, $T_{max} = 0.96$	$h = -13 \rightarrow 13$
11089 measured reflections	$k = -12 \rightarrow 12$
	$l = -15 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$+ 0.6736P]$
$wR(F^2) = 0.094$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
2839 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
205 parameters	$\Delta\rho_{min} = -0.35$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1B⋯O1W	0.91 (2)	2.09 (2)	2.993 (2)	169.9 (19)
N2—H2B⋯O1	0.89 (2)	1.90 (2)	2.7914 (19)	177 (2)
N2—H2A⋯O2^i	0.88 (2)	2.11 (2)	2.932 (2)	153.8 (19)
N3—H3B⋯O2^i	0.90 (2)	2.04 (2)	2.892 (2)	156.1 (19)
N3—H3A⋯O1W^{ii}	0.88 (2)	1.99 (2)	2.863 (2)	175 (2)
O1W—H1WA⋯O1	0.86 (2)	1.88 (2)	2.7157 (18)	164 (2)
O1W—H1WB⋯O2^{iii}	0.86 (2)	1.86 (2)	2.7061 (18)	168 (2)

Symmetry codes: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$.

H atoms bonded to aryl C atoms were included in calculated positions, with C—H distances of 0.95 Å, and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms bonded to O and N atoms were located in difference maps and assigned a common fixed U_{iso} of 0.04 Å^2; their coordinates were freely refined.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL and MERCURY (Bruno et al., 2002); software used to prepare material for publication: SHELXTL.

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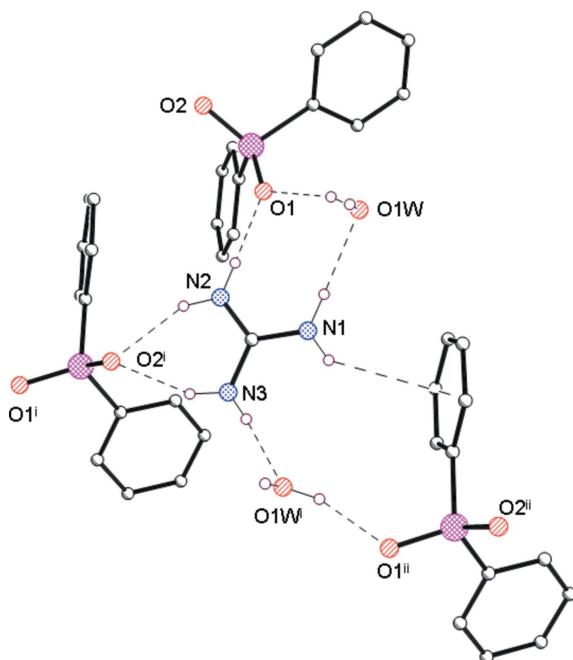Allen, F. H. (2002). Acta Cryst. B**58**, 380–388.

Figure 5
A view of the hydrogen bonding (dashed lines) involving the guanidinium ion. Symmetry codes are as in Table 1. H atoms not involved in hydrogen bonding have been omitted.

3473 cm^{-1} in the IR spectrum; normal hydrogen-bonding will contribute to the broad signal observed at lower frequency.

The phenyl groups are also involved in several intermolecular interactions. The C12–C16 ring, which interacts with the cation as described above, also has a π–π interaction with the C21–C26 ring of a symmetry-related anion at $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$. The planes of the rings are inclined at 2.6 (1)°, and the mean distance of the C21–C26 ring from the mean plane of C11–C16 is 3.530 (2) Å. The centroid-to-centroid distance [4.059 (3) Å] is rather long but the interatomic distances C13—C23 and C14—C22 [3.548 (2) and 3.652 (2), respectively] suggest the π–π interaction is real, although more staggered than the norm. This may be due to constraints imposed by both phenyl rings being part of the superstructure of the same hydrogen-bonded layer. The second face of the C21–C26 ring shows a C—H⋯π interaction with atom H13 [under symmetry operation (vi), $(1 - x, 1 - y, -z)$]; atom H13^{iv} is 2.690 (2) Å from the mean plane of the phenyl ring and 2.695 (2) Å from the centroid of the ring. This appears to be the only significant interbilayer interaction.

In summary, all six guanidinium hydrogen-bond donors of (I) are involved in hydrogen bonding, although one is unconventional. The solvent water molecule makes four hydrogen bonds, two as donor and two as acceptor. One of the phosphinate O atoms acts as acceptor for two hydrogen bonds and the other accepts three [two as part of the $R_2^1(6)$ ring]. All hydrogen-bond donors have acceptors.

Experimental

Diphenylphosphinic acid (Merck; 1 mmol, 0.218 g) was added to an aqueous solution (10 ml) of guanidinum carbonate (Merck; 1 mmol,

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