

Hydrogen bonding in 1-carbamoyl-guanidinium methylphosphonate monohydrate¹

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Received 11 November 2002

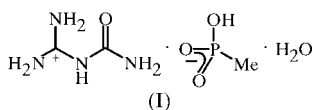
Accepted 13 March 2003

Online 18 April 2003

The title compound, $C_2H_7N_4O^+ \cdot CH_4O_3P^- \cdot H_2O$, crystallized with one carbamoylguanidinium cation, one methylphosphonate anion and one water molecule in the asymmetric unit. All H atoms of the carbamoylguanidinium ion are involved in a hydrogen-bonded network. The $CH_3PO_2(OH)$ anions, together with the water molecules, build O—H...O hydrogen-bonded ribbons around a 2_1 screw axis parallel to the b axis. Neighbouring ribbons are not directly connected *via* hydrogen bonding. The carbamoylguanidinium cations are linked to these ribbons by N—H...O bridges and build a slightly buckled layer structure, the interlayer distance being $b/2$.

Comment

The present study was undertaken in order to reveal the nature of the title compound, (I). The asymmetric unit was found to contain one carbamoylguanidinium (CG) cation, one methylphosphonate (MP) anion and one water molecule. These are shown in Fig. 1, in which the atom-numbering scheme is also defined.



The MP anion has a distorted tetrahedral geometry (Table 1), with bond angles ranging between 106.3 (2) and 113.7 (1)°. The P—C3 bond length is in good agreement with the P—C distances of dimethylphosphinic acid, as reported by Giorando & Ripamonti (1967). The O2—H6 hydroxyl group of the MP anion acts as a donor to O4ⁱ (see Table 2 for symmetry code) of a screw-related anion to form an endless N_1 [equivalent to $C_1^1(4)$] chain (Bernstein *et al.*, 1995), and as

an acceptor of H7A of the water molecule (Fig. 2). This water molecule donates its second H atom to atom O3ⁱⁱ (see Table 2 for symmetry code) of an anion displaced by $-b$ from that of the asymmetric unit, thus forming an N_2 [equivalent to $C_2^2(6)$] chain. Both chains run parallel to the b axis, and the combination of these chains generates a column built from N_3 [equivalent to $R_4^4(12)$] rings (*E* in Fig. 2).

The non-H-atom skeleton of the cation is nearly planar. A dihedral angle of 3.40 (4)° is formed by the normals to the planes of the ureic (C1/N1/N2/O1) and guanidinium (C2/N2/N3/N4) fragments, each of which is planar within experimental error. The bond lengths found in the cation are compared in Table 3 with those reported previously for this moiety; references are indicated by their Cambridge Structural Database codes (Allen, 2002). In general, excellent agreement is found, except that the bond lengths deposited for the low-temperature structure QIRGIH tend to be 0.01–0.02 Å longer. The trend in the bond lengths, such that $N2-C1 > N2-C2 > N1-C1 = N3-C2 = N4-C2$, is well established and is consistent with a low degree of conjugation between the ureic and guanidinium fragments, as noted by Scoconi *et al.* (1991). These authors mentioned that N—C multiple bonding will place formal positive charges on the N atoms and thus enhance their ability to form hydrogen bonds. Indeed, previous studies of the CG cation have shown that all N—H bonds act as proton donors, and this behaviour is also found in the present study.

The CG cation is connected to the MP anion *via* three N—H...O hydrogen bonds, generating two condensed rings [C , $N_2 = R_2^2(6)$, and D , $N_2 = R_2^2(8)$]. Two of the contacts involve atom O3, which is approximately equidistant from atoms H2 and H3A. This situation differs from that described by Zaman & Darlow (1986), in which the corresponding O atom is 0.6 Å closer to H2 than to H3A.

Atom O3 also accepts atom H1Bⁱⁱⁱ (see Table 2 for symmetry code) of a c -glide-related cation. Furthermore, the water molecule accepts atoms H3B and H4A to form a six-membered ring [B , $N_2 = R_2^1(6)$]. These two protons are often donated to a common acceptor, such as a Cl^- ion or an MO_2 fragment of a dinitroamide, phosphate or perchlorate ion. The

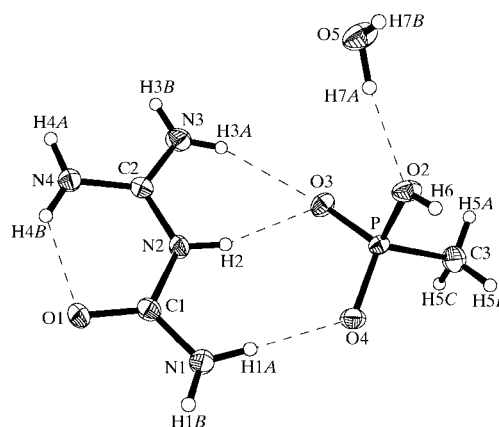


Figure 1

A view of the molecules of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 20% probability level.

¹ Dedicated to the late Professor Dr O. Stelzer.

MO_2 fragments act as bidentate acceptors, forming $N_2 [R_2^2(8)]$ rings.

A strong intramolecular $N-H \cdots O$ hydrogen bond ($H4B \cdots O1$) closes a six-membered ring [A , $N_1 = S(6)$]. This motif of intramolecular hydrogen bridging has been encountered frequently (Bilton *et al.*, 2000) and has always been found in structure determinations of the CG cation (Begley *et al.*, 1985, 1988; Bemm, 2000; Scoponi *et al.*, 1991; Zaman & Darlow, 1986).

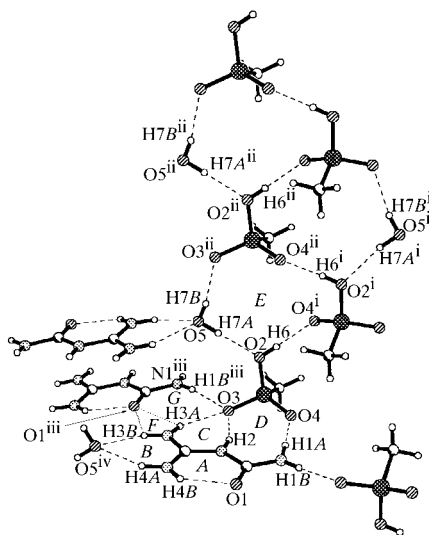


Figure 2

A view of the asymmetric unit and surrounding molecules of (I), showing the hydrogen-bonding network. The ring labels A–G are defined in the Comment.

In addition to these strong interactions, $O1^{iii}$ makes two weak contacts with $H3A$ and $H3B$ to build a four-membered [F , $N_2 = R_2^1(4)$] and a six-membered [G , $N_3 = R_2^2(6)$] ring, respectively. In more than half of the reported structures of the CG cation, intermolecular $O1 \cdots H3A$ hydrogen bonding strongly links the cations in chains in a head-to-tail fashion. In (I), this motif is disrupted by the strong interaction with the anion. Details of the hydrogen bonding are collected in Table 2.

Experimental

The title compound was obtained from Clariant GmbH, Germany. Colourless crystals were obtained by slow evaporation of water from a concentrated solution. In the $^{13}C\{^1H\}$ NMR spectrum, (I) shows three signals. The two singlets at δ values of 155.5 and 156.2 p.p.m. can be assigned to the carbamoyl and guanidinium C atoms of the cation. The chemical shifts are in good agreement with the values reported by Hesse *et al.* (1991), Kalinowski *et al.* (1984a) and Machnitzki *et al.* (2000). The signal at a δ value of 15.3 p.p.m., showing a doublet fine structure [$^1J(PC) = 135.3$ Hz], corresponds to the C atom of the methylphosphonate anion. The chemical shift and coupling constant agree well with those reported by Berger *et al.* (1993) and Kalinowski *et al.* (1984b) for diethyl methylphosphonate and related compounds. The $^{13}C\{^1H\}$ NMR spectrum was recorded on a Bruker ARX 400 spectrometer at 100.6 MHz using d_6 -dimethyl sulfoxide as solvent.

Crystal data

$C_5H_7N_4O^+ \cdot CH_4O_3P^- \cdot H_2O$
 $M_r = 216.14$
 Monoclinic, $P2_1/c$
 $a = 11.9081$ (18) Å
 $b = 6.4458$ (7) Å
 $c = 13.996$ (3) Å
 $\beta = 111.440$ (16)°
 $V = 999.9$ (3) Å³
 $Z = 4$
 $D_x = 1.436$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 50 reflections
 $\theta = 10.8$ – 14.4°
 $\mu = 0.28$ mm⁻¹
 $T = 295$ (2) K
 Prism, colourless
 $0.46 \times 0.29 \times 0.28$ mm

Data collection

Siemens P3 diffractometer
 ω scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{min} = 0.883$, $T_{max} = 0.926$
 2400 measured reflections
 2293 independent reflections
 1467 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.025$

$\theta_{max} = 27.5^\circ$
 $h = 0 \rightarrow 15$
 $k = 0 \rightarrow 8$
 $l = -18 \rightarrow 16$
 3 standard reflections every 100 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.085$
 $S = 0.83$
 2293 reflections
 171 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.28$ e Å⁻³
 $\Delta\rho_{min} = -0.23$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0119 (12)

Table 1

Selected geometric parameters (Å, °).

P–O2	1.5714 (17)	P–O4	1.5042 (15)
P–O3	1.5055 (14)	P–C3	1.774 (3)
O2–P–O3	106.36 (9)	O1–C1–N1	125.0 (2)
O2–P–O4	110.07 (9)	O1–C1–N2	121.6 (2)
O3–P–O4	113.70 (10)	N1–C1–N2	113.4 (2)
O2–P–C3	106.26 (15)	N2–C2–N3	117.5 (2)
O3–P–C3	110.98 (14)	N2–C2–N4	121.60 (19)
O4–P–C3	109.18 (12)	N3–C2–N4	120.9 (2)
C2–N2–C1	126.19 (18)		

Table 2

Hydrogen-bonding and short-contact geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O2-H6 \cdots O4^i$	0.78 (3)	1.76 (3)	2.533 (2)	172 (3)
$O5-H7A \cdots O2$	0.88 (4)	1.96 (4)	2.810 (3)	164 (3)
$O5-H7B \cdots O3^{ii}$	0.82 (3)	1.99 (3)	2.800 (3)	170 (3)
$N1-H1A \cdots O4$	0.87 (3)	1.99 (3)	2.859 (3)	175 (2)
$N1^{iii}-H1B^{iii} \cdots O3$	0.85 (2)	2.12 (2)	2.959 (3)	172 (2)
$N2-H2 \cdots O3$	0.86 (2)	2.14 (3)	2.969 (3)	161 (2)
$N3-H3A \cdots O1^{iii}$	0.83 (2)	2.62 (2)	2.897 (2)	101 (2)
$N3-H3A \cdots O3$	0.83 (2)	2.22 (3)	2.997 (3)	158 (2)
$N3-H3B \cdots O1^{iii}$	0.87 (3)	2.64 (2)	2.897 (2)	98 (2)
$N3-H3B \cdots O5^{iv}$	0.87 (3)	2.06 (3)	2.850 (3)	151 (2)
$N4-H4A \cdots O5^{iv}$	0.92 (3)	2.08 (3)	2.918 (3)	151 (2)
$N4-H4B \cdots O1$	0.84 (2)	2.01 (2)	2.664 (3)	134 (2)

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

Table 3
Bond lengths (Å) for 1-carbamoylguanidinium cations.

Reference	C1–O	C1–N1	C1–N2	C2–N2	C2–N3	C2–N4
(I) [†]	1.224 (2)	1.324 (3)	1.402 (3)	1.349 (3)	1.309 (3)	1.319 (3)
DIVVEJ [‡]	1.225 (3)	1.326 (4)	1.392 (4)	1.358 (4)	1.318 (3)	1.313 (3)
DUNHID [§]	1.217 (3)	1.329 (3)	1.399 (3)	1.358 (3)	1.319 (3)	1.320 (3)
GADWUD [¶]	1.233 (5)	1.319 (5)	1.390 (4)	1.355 (4)	1.323 (5)	1.304 (5)
JODZOR1 ^{††}	1.221 (3)	1.326 (3)	1.395 (3)	1.356 (3)	1.322 (3)	1.313 (3)
JODZOR2 ^{††}	1.225 (3)	1.319 (3)	1.394 (2)	1.356 (3)	1.318 (2)	1.304 (3)
QIRGIH ^{‡‡}	1.236 (2)	1.336 (2)	1.415 (2)	1.371 (2)	1.331 (2)	1.323 (2)

[†] This work. [‡] Begley *et al.* (1985). [§] Zaman & Darlow (1986). [¶] Begley *et al.* (1988). ^{††} Scoconi *et al.* (1991). ^{‡‡} Bemm (2000).

H-atom positions were located from difference Fourier maps and were individually refined, as were the respective U_{iso} values. Refined C–H distances were in the range 0.92 (3)–0.96 (3) Å.

Data collection: *P3/PC* (Siemens, 1992); cell refinement: *P3/PC*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS93* (Sheldrick, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1047). Services for accessing these data are described at the back of the journal.

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