

***N,N'*-Dimethylpiperazinium(2+) phosphonoacetate: hydrogen-bonded anion sheets containing cation-templated $R_6^6(28)$ rings**Dorcas M. M. Farrell,^a George Ferguson,^{a†} Alan J. Lough^b and Christopher Glidewell^{a*}^aSchool of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, and ^bLash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 3H6

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Received 4 May 2001

Accepted 14 May 2001

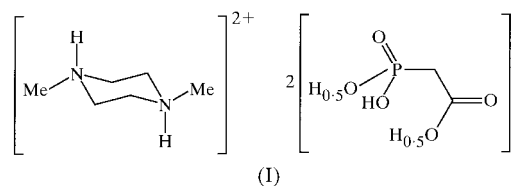
In the title compound, $C_6H_{16}N_2^{2+} \cdot 2C_2H_4O_5P^-$, the cations lie across centres of inversion; in the anions, two of the H-atom sites have 0.50 occupancy. The anions are linked by short O—H \cdots O hydrogen bonds [O \cdots O 2.465 (3)–2.612 (3) Å and O—H \cdots O 165–171°] into sheets of alternating $R_2^2(12)$ and $R_6^6(28)$ rings, both of which are centrosymmetric; the cations lie at the centres of the larger rings linked to the anion sheet by N—H \cdots O hydrogen bonds [N \cdots O 2.642 (2) Å and N—H \cdots O 176°].

Comment

Phosphonic acids are extremely versatile building blocks in supramolecular chemistry (Ferguson *et al.*, 1998; Glidewell *et al.*, 2000; Wheatley *et al.*, 2001). An important factor in the behaviour of such acids is the marked difference in acidity of the two hydroxyls in the $-PO(OH)_2$ group, such that with organic amines typically only one H atom per phosphonate is transferred from O to N. The resulting $-P(O)_2(OH)^-$ group can thus act both as a hydrogen-bond donor and as a hydrogen-bond acceptor. In this respect, singly ionized phosphonate groups are qualitatively different from ionized carboxyl groups, which can act only as hydrogen-bond acceptors. Seeking to combine, and compare, these two functionalities, we have turned our attention to phosphonoacetic acid, $(HO)_2P(O)CH_2COOH$.

The structure of phosphonoacetic acid itself [Cambridge Structural Database (CSD; Allen & Kennard, 1993) code TERLUX (Lis, 1997)] contains a three-dimensional hydrogen-bonded framework, dominated by $C(4)$ and $C(6)$ spiral motifs around the screw axes in space group $P2_12_12_1$; however, the $R_2^2(8)$ motif, so characteristic of carboxylic acids (Sim *et al.*, 1955; Bruno & Randaccio, 1980), as well as phenylphosphonic

acid itself (Weakley, 1976), is absent. Rather few examples have been reported of phosphonoacetate salts of other organic moieties. In the 1:1 salt formed with 2-amino-5-nitropyridine (CSD code YISDOT; Pécaud & Masse, 1994), the $C_2H_4O_5P^-$ anions are built into sheets by just two rather short O—H \cdots O hydrogen bonds, having O \cdots O distances of 2.600 (2) and 2.630 (2) Å, and these sheets are linked into a three-dimensional framework by the cations. However, the coordinates in the original paper, and in the CSD, do not represent a connected molecular unit, and those for at least one of the hydroxyl H atoms are seriously in error; hence, detailed analysis of the sheet formation is not appropriate.



The 1:1 adduct (I) formed between *N,N'*-dimethylpiperazine and phosphonoacetic acid is a salt, $[[MeN(CH_2CH_2)_2NMe]H_2]^{2+} \cdot 2[C_2H_4O_5P]^-$ (Fig. 1). The cation lies across a centre of inversion, selected for the sake of convenience as that at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, while the anion lies in a general position. The ionization of the anion is not straightforward: there is a fully occupied H-atom site adjacent to O3, but the H-atom sites adjacent to O2 and O4 are both half-occupied. Pairs of O2 atoms are linked across centres of inversion; O2 at (x, y, z) acts either as donor to, or as acceptor from, O2 at $(2-x, -y, 3-z)$, also referred to as *i*), while O4 at (x, y, z) acts as donor to or acceptor from O4 at $(1-x, 1-y, 2-z)$, also referred to as *iii*). In both interactions, the O \cdots O distances are very short, < 2.50 Å (Table 2), approaching the distances typical in O \cdots H \cdots O hydrogen bonds where the H atom is symmetrically centred between the O atoms (Emsley, 1980). However, for both examples here, involving O2 and O4, careful inspection of difference maps showed clearly that there were two equally occupied off-centre sites.

The O—H \cdots O hydrogen bonds (Table 2) link the anions into a two-dimensional sheet built from alternating $R_2^2(12)$ and $R_6^6(28)$ rings. Phosphonate O3 at (x, y, z) acts as hydrogen-bond donor to carboxyl O1 at $(2-x, -y, 2-z)$, thus producing an $R_2^2(12)$ ring centred at $(1, 0, 1)$ (Fig. 2). The O2 \cdots O2^{*i*} hydrogen bond links this dimer centred at $(1, 0, 1)$ to similar dimers centred at $(1, 0, 0)$ and $(1, 0, 2)$, while the O4 \cdots O4^{*iii*} hydrogen bond links the reference $(1, 0, 1)$ dimer to those centred at $(0, 1, 1)$ and $(2, \bar{1}, 1)$. Propagation of the hydrogen bonds by translation thus generates a (110) sheet of anions containing just two types of ring (Fig. 2). The sheets are weakly linked by a single C—H \cdots O hydrogen bond (Table 2). The $R_2^2(12)$ rings are all centred at the vertices of the unit cell and the $R_6^6(28)$ rings are centred at the cell centres, where the cations are located. The two N atoms in the cation centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ are at (x, y, z) and $(1-x, 1-y, 1-z)$ and these act as hydrogen-bond donors to O5 atoms, also at (x, y, z) and $(1-x, 1-y, 1-z)$, respectively, on opposite sides of the $R_6^6(28)$ rings (Fig. 2).

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The sheet structure formed by the anions in (I) may be contrasted with the anion aggregation in the corresponding anhydrous lithium and ammonium salts. In the lithium salt (CSD code TERMOS; Lis, 1997), the anions are linked into head-to-head chains containing centrosymmetric $R_2^2(8)$ rings formed by the phosphonate units in adjacent anions and centrosymmetric $R_2^2(12)$ rings formed by carboxyl donor and phosphonate acceptors; as in the parent acid, the carboxyl $R_2^2(8)$ motif is absent. By contrast, in the ammonium salt (CSD code TERMIM; Lis, 1997), the anions are linked into sheets formed by linking $R_2^2(8)$ phosphonate dimers. As noted above this motif is absent in compound (I), where the large rings may be regarded as templated by the cations.

The three independent P—O distances show marked variation (Table 1): P1—O3, which is associated with the fully ordered H atom is the longest and P1—O5, with no H-atom

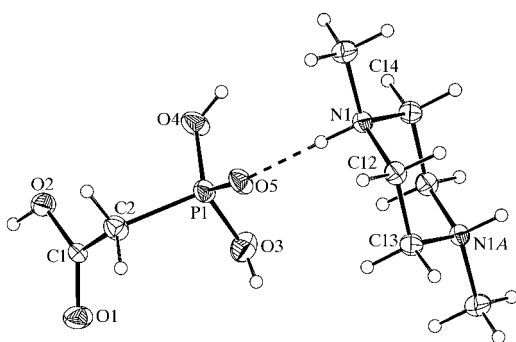


Figure 1

The molecular components of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atom marked A is at the symmetry position $(1-x, 1-y, 1-z)$, and the H-atom sites adjacent to O2 and O4 both have 0.50 occupancy.

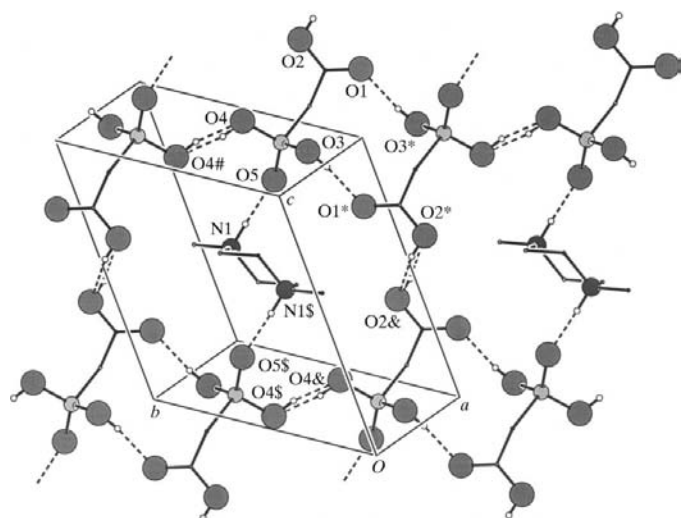


Figure 2

Part of the crystal structure of (I) showing the formation of a (110) sheet of anions with the cations at the centres of the $R_6^0(28)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms labelled with an asterisk (*), hash (#), dollar sign (\$) or ampersand (&) are at the symmetry positions $(2-x, -y, 2-z)$, $(1-x, 1-y, 2-z)$, $(1-x, 1-y, -z)$ and $(x, y, -1+z)$, respectively.

involvement, is the shortest. Similarly, C1—O1, with no H-atom involvement, is significantly shorter than C1—O2, associated with a disordered H atom. The O—P—O and O—C—O angles also reflect the H-atom site occupancies. The O1—C1—O2 and C1—C2—P1 planes are approximately orthogonal, while O5 is antiperiplanar to the carboxyl group (Table 1). In the cation, the methyl groups occupy equatorial sites, as expected, and the three independent C—N distances are identical within experimental uncertainty.

Experimental

Stoichiometric quantities of phosphonoacetic acid and N,N' -dimethylpiperazine were separately dissolved in methanol. The solutions were mixed and the resulting mixture set aside to crystallize, producing analytically pure (I). Analysis, found: C 30.5, H 6.2, N 7.1%; $C_{10}H_{24}N_2O_{10}P_2$ requires: C 30.5, H 6.1, N 7.1%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$C_6H_{16}N_2^{2+} \cdot 2C_2H_4O_5P^-$
 $M_r = 394.25$
 Triclinic, $P\bar{1}$
 $a = 5.9217(4) \text{ \AA}$
 $b = 8.9858(5) \text{ \AA}$
 $c = 8.9987(6) \text{ \AA}$
 $\alpha = 61.730(3)^\circ$
 $\beta = 81.885(3)^\circ$
 $\gamma = 81.448(4)^\circ$
 $V = 415.65(5) \text{ \AA}^3$

$Z = 1$
 $D_x = 1.575 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 1719 reflections
 $\theta = 2.7\text{--}27.6^\circ$
 $\mu = 0.32 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Plate, colourless
 $0.34 \times 0.20 \times 0.06 \text{ mm}$

Data collection

KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan
 (DENZO-SMN; Otwinowski & Minor, 1997)
 $T_{\min} = 0.900$, $T_{\max} = 0.981$
 5103 measured reflections
 1900 independent reflections

1320 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 27.6^\circ$
 $h = 0 \rightarrow 7$
 $k = -11 \rightarrow 11$
 $l = -11 \rightarrow 11$
 Intensity decay: negligible

Table 1

Selected geometric parameters (\AA , $^\circ$).

N1—C12	1.490 (3)	C1—C2	1.473 (3)
N1—C13 [†]	1.492 (3)	C2—P1	1.811 (2)
N1—C14	1.492 (3)	P1—O3	1.562 (2)
C12—C13	1.506 (3)	P1—O4	1.5168 (18)
O1—C1	1.252 (3)	P1—O5	1.4874 (19)
O2—C1	1.293 (3)		
O3—P1—O4	106.38 (12)	O3—P1—C2	106.20 (12)
O4—P1—O5	115.41 (11)	O4—P1—C2	107.96 (12)
O5—P1—O3	112.35 (11)	O5—P1—C2	108.09 (11)
O1—C1—C2	122.2 (2)	O1—C1—O2	121.0 (2)
O2—C1—C2	116.8 (2)	C1—C2—P1	114.59 (18)
O3—P1—C2—C1	−48.8 (2)	O1—C1—C2—P1	96.6 (2)
O4—P1—C2—C1	64.9 (2)	O2—C1—C2—P1	−83.6 (2)
O5—P1—C2—C1	−169.60 (18)		

Symmetry code: (i) $1-x, 1-y, 1-z$.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.125$
 $S = 1.04$
 1900 reflections
 114 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0458P)^2 + 0.1391P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.034$
 $\Delta\rho_{\max} = 0.26 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.39 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 (Sheldrick, 1997)
 Extinction coefficient: 0.021 (7)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1 \cdots O5$	0.91	1.73	2.642 (2)	176
$O2-H2 \cdots O2^i$	0.82	1.72	2.494 (4)	158
$O3-H3 \cdots O1^{ii}$	0.82	1.80	2.612 (3)	171
$O4-H4 \cdots O4^{iii}$	0.82	1.66	2.465 (3)	165
$C12-H12A \cdots O5^{iv}$	0.97	2.46	3.203 (3)	133

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

Compound (I) crystallized in the triclinic system; space group $P\bar{1}$ was assumed and confirmed by the analysis. H atoms were treated as riding atoms with a C—H distance of 0.96 (CH₃) or 0.97 Å (CH₂), an N—H distance of 0.91 Å and an O—H distance of 0.82 Å.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97*

(Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC Canada.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1482). Services for accessing these data are described at the back of the journal.

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