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rac-1-Phenylethylammonium carboxymethylphosphonate(1−): hydrogen-bonded anion sheets with pendent cations

David E. Turkington,[a] George Ferguson,[a]‡ Alan J. Lough[b] and Christopher Glidewell[a]*

[a]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland, and [b]Lash Miller Chemical Laboratories, University of Toronto, Ontario, Canada M5S 3H6
Correspondence e-mail: cg@st-andrews.ac.uk

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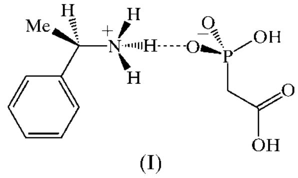
In the title compound, $C_8H_{12}N^+\cdot C_2H_4O_5P^-$, the anions are linked by two O—H···O hydrogen bonds [H···O both 1.75 Å, O···O = 2.5781 (15) and 2.5834 (15) Å, and O—H···O = 169 and 176°] into sheets built from alternating $R_2^2(8)$ and $R_6^6(32)$ rings. Each cation is linked to an anion sheet by three N—H···O hydrogen bonds [H···O = 1.88–2.04 Å, N···O = 2.7603 (16)–2.9334 (17) Å and N—H···O = 162–166°], such that all the cations pendent from one face of the sheet are of the *R* configuration, while all those pendent from the opposite face are of the *S* configuration.

Comment

The structures of carboxymethylphosphonic acid [$HOOCCH_2P(O)(OH)_2$] and its ammonium salt ($NH_4^+\cdot C_2H_4O_5P^-$) were reported several years ago (Lis, 1997), and since then the supramolecular structures have been reported for a number of salts formed by reaction of this acid with a range of organic diamines (Farrell *et al.*, 2001; Videnova-Adrabinska, 2002; Bowes *et al.*, 2003). We report here the supramolecular structure of the salt, (I), formed with a racemic chiral monoamine, *viz.* 1-phenylethylamine.



(I)

In (I), $[PhCH(CH_3)NH_3]^+\cdot[HOOCCH_2P(O)_2OH]^-$ (Fig. 1), one H atom has been fully transferred to the amine from a POH unit of the acid. In the anion, the C—O and P—O distances (Table 1) are fully consistent with the locations of the associated H atoms as deduced from difference maps. The O—P—O angle involving the two unprotonated O atoms (O3 and O4) is significantly larger than the other O—P—O angles, and it is balanced by a correspondingly small O5—P1—C2 angle. The remaining bond distances and interbond angles show no unusual features. The centrosymmetric space group accommodates equal numbers of *R* and *S* cations, and the asymmetric unit was selected to include a cation of the *R* configuration.

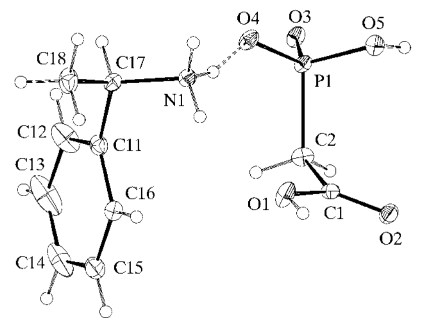


Figure 1
The independent components of (I), showing the *R* enantiomorph of the cation, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

The two-dimensional anion substructure is readily analysed in terms of the actions of the two independent O—H···O hydrogen bonds (Table 2), and it is convenient to consider these in turn. Phosphonate atom O5 in the anion at (x, y, z) acts as a hydrogen-bond donor to phosphonate atom O3 in the anion at ($1-x$, $1-y$, $1-z$), so generating a centrosymmetric $R_2^2(8)$ ring centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). The action of the second O—H···O hydrogen bond is then readily analysed in terms of the linking of the $R_2^2(8)$ dimers. Carboxy atoms O1 in the anions at (x, y, z) and ($1-x$, $1-y$, $1-z$), which form the ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) dimer, act as hydrogen-bond donors to phosphonate atoms O4 at (x, $\frac{1}{2}-y$, $-\frac{1}{2}+z$) and ($1-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$), respectively, which are themselves components of the dimers centred at ($\frac{1}{2}$, 0, 0) and ($\frac{1}{2}$, 1, 1), respectively. Similarly, the two O4 atoms in the ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) dimer accept hydrogen bonds from carboxy atoms O1 in the anions at (x, $\frac{1}{2}-y$, $\frac{1}{2}+z$) and ($1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$), themselves components of the dimers centred at ($\frac{1}{2}$, 0, 1) and ($\frac{1}{2}$, 1, 0), respectively.

In this way, the two O—H···O hydrogen bonds generate a (100) sheet of anions built from alternating $R_2^2(8)$ and $R_6^6(32)$ rings, where both ring types are centrosymmetric (Fig. 2). The $R_2^2(8)$ rings are centred at ($\frac{1}{2}$, m, n) and ($\frac{1}{2}$, $m+\frac{1}{2}$, $n+\frac{1}{2}$), and the $R_6^6(32)$ rings are centred at ($\frac{1}{2}$, m, $n+\frac{1}{2}$) and ($\frac{1}{2}$, $m+\frac{1}{2}$, n) (where m and n independently take the value zero or integer). A single sheet of this type passes through each unit cell. The two-dimensional anion substructure of (I) is thus the same as that observed in the imidazolium salt (Videnova-Adrabinska, 2002), but differs from that found in the salt formed with 1,2-bis(4′-pyridyl)ethane, where the anion sheets consist of alternating $R_2^2(12)$ and $R_6^6(28)$ rings (Bowes *et al.*, 2003). A more common occurrence of the $R_2^2(8)$ motif in salts with diamines is

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‡ Permanent address: Department of Chemistry, University of Guelph, Ontario, Canada N1G 2W1.

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as a component of one-dimensional anion substructures including chains of spiro-fused rings and chains of edge-fused rings (Bowes *et al.*, 2003).

The cation in (I) is linked to the anion sheet in a multi-point interaction; the acceptors in the three N—H···O hydrogen bonds are provided to three different anions, all lying in the same (100) sheet (Table 2). Because the anion sheet is centrosymmetric, all of the cations pendent from one face of the sheet have the *R* configuration, while all those pendent from the opposite face of the same sheet have the *S* configuration. Two cations, one *R* and one *S*, lie over each $R^6_6(32)$ ring and their effect is to divide this ring into five sectors, *viz.* one centrosymmetric $R^4_6(16)$ ring, two $R^2_3(10)$ rings and two $R^3_3(12)$ rings (Fig. 2). The (100) sheet is thus tripartite in nature, with a polar central layer between lipophilic outer layers comprising methyl and phenyl groups (Fig. 3). A similar overall structure was observed in the imidazolium salt, although with only two-point attachment of the cations to the anion sheet.

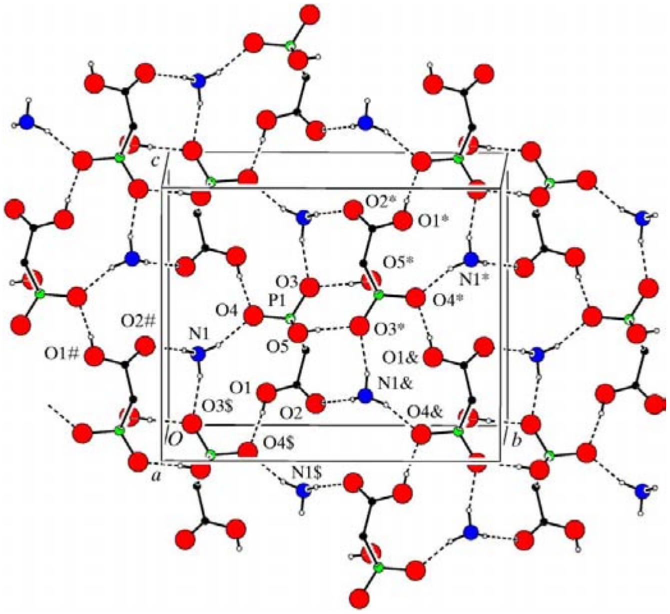

Figure 2
Part of the crystal structure of (I), showing (*a*) the formation of the anion sheet and (*b*) the linking of the cations to the anion sheet. For clarity, the hydrocarbyl component of the cations and H atoms bonded to C atoms in the anions have been omitted. Atoms marked with an asterisk (*), a hash (#), a dollar sign ($) or an ampersand (&) are at the symmetry positions $(1-x, 1-y, 1-z)$, $(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, $(x, \frac{1}{2}-y, -\frac{1}{2}+z)$ and $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$, respectively.

Adjacent (100) sheets are linked weakly by a single C—H···π(arene) hydrogen bond (Table 2); atom C2 in the anion at (x, y, z), part of the sheet centred at $x = \frac{1}{2}$, acts as a hydrogen-bond donor, *via* atom H2*B*, to the phenyl ring of the cation at $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$, which forms part of the sheet centred at $x = -\frac{1}{2}$. Propagation by inversion of this interaction links all of the (100) sheets into a single three-dimensional framework.

All of the hard (Desiraju & Steiner, 1999) hydrogen bonds in (I) have *D*—H···*A* units that are almost linear and the O—H···O hydrogen bonds are short for their type. It remains a moot point whether the formation of the anion substructure is controlled primarily by the short strong O—H···O hydrogen bonds or whether the cations provide some significant direction to the structure-assembly process; the formation of the same anion substructure in the presence of two very different cations, *viz.* imidazolium and 2-phenylethylammonium, perhaps argues against the cation-template effect previously suggested (Videnova-Adrabinska, 2002).

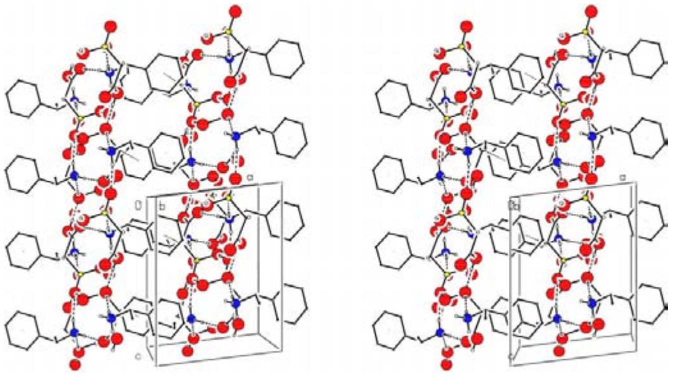

Figure 3
A stereoview of part of the crystal structure of (I), showing the tripartite nature of the (100) sheets and the C—H···π(arene) hydrogen bond linking adjacent sheets. For clarity, H atoms bonded to C atoms but not involved in the motif shown have been omitted.

Experimental

Equimolar quantities of racemic 1-phenylethylamine and carboxymethylphosphonic acid were dissolved separately in methanol. The solutions were mixed and the mixture was then set aside to crystallize, providing analytically pure (I). Analysis found: C 45.9, H 6.6, N 5.7%; $C_{10}H_{16}NO_5P$ requires: C 46.0, H 6.2, N 5.4%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the prepared sample.

Crystal data

$C_8H_{12}N^+ \cdot C_2H_4O_5P^-$
$M_r = 261.21$
Monoclinic, $P2_1/c$
$a = 8.2969$ (3) Å
$b = 13.6898$ (3) Å
$c = 11.0388$ (4) Å
$\beta = 96.7869$ (18)°
$V = 1245.03$ (7) Å^3
$Z = 4$
$D_x = 1.394$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 2845 reflections
$\theta = 2.9$–$27.5°$
$\mu = 0.23$ mm^{-1}
$T = 150$ (1) K
Plate, colourless
0.28 × 0.18 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
10 538 measured reflections
2845 independent reflections
2394 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\max} = 27.5°$
$h = -10 \rightarrow 10$
$k = -15 \rightarrow 17$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.095$
$S = 1.05$
2845 reflections
159 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 0.6945P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0076 (19)

Table 1
Selected geometric parameters (Å, °).

P1—O3	1.5088 (11)	P1—C2	1.8137 (16)
P1—O4	1.5043 (11)	C1—O1	1.3120 (18)
P1—O5	1.5667 (11)	C1—O2	1.2167 (19)
O3—P1—O4	115.10 (6)	O3—P1—C2	107.18 (7)
O4—P1—O5	107.79 (6)	O4—P1—C2	109.99 (7)
O5—P1—O3	111.51 (6)	O5—P1—C2	104.79 (7)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1⋯O4^{i}	0.84	1.75	2.5781 (15)	169
O5—H5⋯O3^{ii}	0.84	1.75	2.5834 (15)	176
N1—H1*A*⋯O4	0.91	1.88	2.7603 (16)	164
N1—H1*B*⋯O3^{i}	0.91	1.95	2.8293 (16)	162
N1—H1*C*⋯O2^{iii}	0.91	2.04	2.9334 (17)	166
C2—H2*B*⋯*Cg*1^{iv}	0.99	2.75	3.6417 (19)	150

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

Space group $P2_1/c$ was uniquely assigned from the systematic absences. All H atoms were located from difference maps and were thereafter treated as riding atoms, with C—H distances of 0.95 (aromatic), 0.98 (CH_3), 0.99 (CH_2) and 1.00 Å (aliphatic CH), N—H distances of 0.91 Å and O—H distances of 0.84 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997) and *PRPKAPPA* (Ferguson, 1999).

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1696). Services for accessing these data are described at the back of the journal.

References

Bowes, K. F., Ferguson, G., Lough, A. J., Zakaria, C. M. & Glidewell, C. (2003). *Acta Cryst.* B**59**, 87–99.

Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond*, pp. 86–89. Oxford University Press.

Farrell, D. M. M., Ferguson, G., Lough, A. J. & Glidewell, C. (2001). *Acta Cryst.* C**57**, 952–954.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.

Lis, T. (1997). *Acta Cryst.* C**53**, 28–42.

Nonius (1997). *KappaCCD Server Software.* Windows 3.11 Version. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Videnova-Adrabinska, V. (2002). *J. Mater. Chem.* **12**, 2931–2935.