

Supramolecular structures of three
configurational isomers of 1-phenyl-
ethanaminium malate(1-)David E. Turkington,^a George Ferguson,^{a†} Alan J. Lough^b
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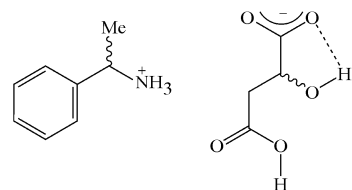
In *rac*-1-phenylethanaminium *rac*-malate(1-), $C_8H_{12}N^+ \cdot C_4H_5O_5^-$, (I), the anions are linked by two inter-anion O—H...O hydrogen bonds into sheets generated by a glide plane and hence containing both enantiomers of the anion. The cations are linked to the anion sheets by three N—H...O hydrogen bonds, such that cations of *R* configuration are bonded to one face of the sheet and cations of *S* configuration are bonded to the other face. In (*R*)-1-phenylethanaminium (*S*)-malate(1-), $C_8H_{12}N^+ \cdot C_4H_5O_5^-$, (III), the anions are again linked by two O—H...O hydrogen bonds, in one of which the H atom is disordered over two sites, into sheets very similar to those in (I) but which are generated in (III) by translation and so contain only a single enantiomer. The cations in (III) are linked to the anion sheets by three N—H...O hydrogen bonds, but the cations are bonded to only one face of the anion sheet. Co-crystallization of (*R*)-1-phenylethanamine with *rac*-malic acid gives the salt (*R*)-1-phenylethanaminium malate(1-), $C_8H_{12}N^+ \cdot C_4H_5O_5^-$, (II), with a structure very similar to that of (III) but where only *ca* 75% of the anion sites are occupied by (*S*)-malate(1-), with the remaining 25% occupied by (*R*)-malate(1-). The layers in (II) show a significant displacement along the [001] direction compared with those in (III).

Comment

We have recently compared the supramolecular structures of pairs of salts formed from achiral diamines and either racemic malic acid or the enantiopure (*S*)-malic acid (Farrell *et al.*, 2002*b*). In these salts, there is a marked tendency for those containing just a single enantiomer of the anion to mimic rather closely the centrosymmetric structures adopted by the corresponding salts formed by the racemic acid. Entirely comparable observations have been made with similar series

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of diamine salts formed from either racemic tartaric acid or enantiopure (*2R,3R*)-tartaric acid (Farrell *et al.*, 2002*a*). We



- (I) *rac*-cation + *rac*-anion
(II) (*R*)-cation + (*R*)-anion/(*S*)-anion (~1:3)
(III) (*R*)-cation + (*S*)-anion

have now extended this general study to encompass systems in which the amine component is also chiral and for this purpose we have selected 1-phenylethanamine, $PhCH(CH_3)NH_2$, which is readily available in both racemic and enantiopure forms. Using this amine and malic acid, $C_4H_6O_5$, we have now prepared the series of 1:1 salts $PhCH(CH_3)NH_3^+ \cdot C_4H_5O_5^-$, using firstly racemic malic acid with both the racemic amine, giving product (I), and the enantiopure (*R*)-amine, giving product (II), and secondly, enantiopure (*S*)-malic acid with each of enantiopure (*R*)-amine, giving product (III), enantiopure (*S*)-amine, giving product (IV), and the racemic amine, giving product (V). Finally, we have also prepared

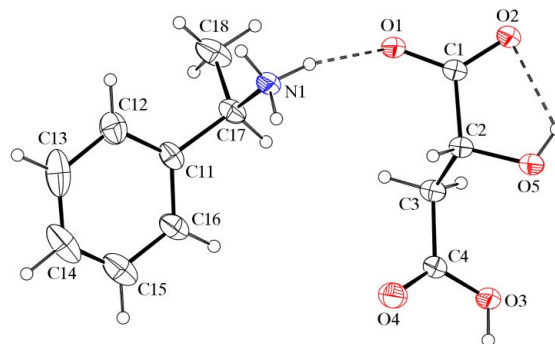


Figure 1

The *R* enantiomers of the independent components in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

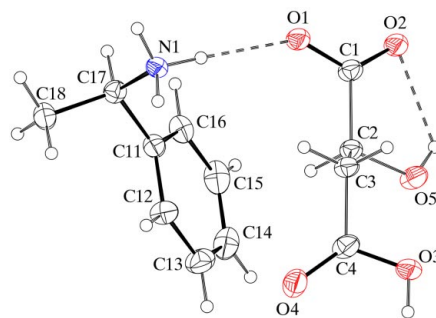


Figure 2

The independent components in (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. For the sake of clarity, only the major enantiomer of the anion is shown.

a single example of a 2:1 salt, *viz.* $2\text{PhCH}(\text{CH}_3)\text{NH}_3^+ \cdot \text{C}_4\text{H}_4\text{O}_5^{2-}$, (VI), using the racemic amine and enantiopure (*S*)-malic acid. Although all six products were readily obtainable in analytically pure form, only (I)–(III) have so far provided crystals suitable for single-crystal X-ray diffraction. We report here the structures of the three isomeric forms, (I)–(III), of 1-phenylethanaminium malate(1-), $\text{C}_8\text{H}_{12}\text{N}^+ \cdot \text{C}_4\text{H}_5\text{O}_5^-$, which all have the same composition, but the constitutions and configurations of which are all different. A previous study of a deuterated form of (III) (Bau *et al.*, 1983) was aimed solely at establishing the stereochemical configuration of an enzyma-

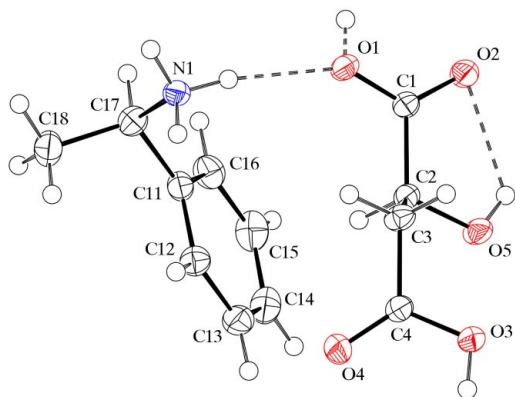


Figure 3

The independent components in (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. In the anion, the H-atom sites adjacent to atoms O1 and O3 have occupancies of 0.13 (4) and 0.87 (4), respectively.

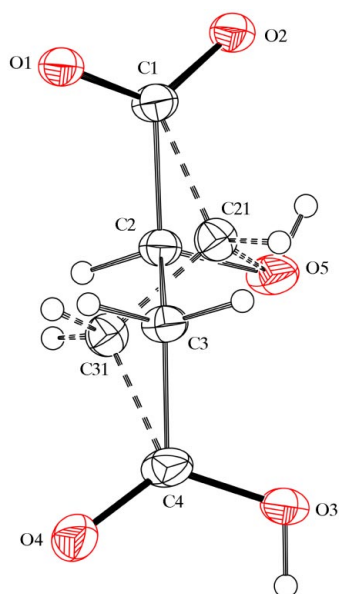


Figure 4

The two enantiomers of the anion in (II). The bonds in the major enantiomer [occupancy 0.745 (8)] are shown as full lines and the bonds unique to the minor enantiomer [occupancy 0.255 (8)] are shown as dashed lines (see text). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

tically produced malic acid containing a CHD group, and hence the absolute stereochemistry of the enzymatic formation of malic acid; no details of the supramolecular structure were given. Here, we discuss first the structure of (I) and then, for the sake of convenience, the structure of (III) before that of (II).

Compound (I), prepared from racemic 1-phenylethanamine and racemic malic acid, crystallizes in the polar space group *Cc*, with equal numbers of *R* and *S* cations and equal numbers of *R* and *S* anions in the unit cell. In the selected asymmetric unit (Fig. 1), both ions have the *R* configuration. Compound (II) (Fig. 2) was prepared using enantiopure (*R*)-1-phenylethanamine and racemic malic acid. This compound crystallizes in space group *P2*₁, but while all the cations have the *R* configuration, the anion sites are occupied by an approximately 1:3 mixture of (*R*)-malate and (*S*)-malate anions, so there has been some selectivity during the crystallization process, with the (*S*)-malate anions preferred. In compound (III) (Fig. 3), which was prepared from two enantiopure components, the *R* amine and the *S* acid, and which also crystallizes in the chiral space group *P2*₁, only these components are present. Hence, the dominant configuration of the anion is the same in (II) and (III), while the same single enantiomer of the cation is present in both (II) and (III). However, while the supramolecular structures of (II) and (III) are similar, they differ in detail.

In each compound, one H atom has been transferred from the acid to the amine to form the cation $[\text{PhCH}(\text{CH}_3)\text{NH}_3]^+$. While the H atoms are all fully ordered in compounds (I) and

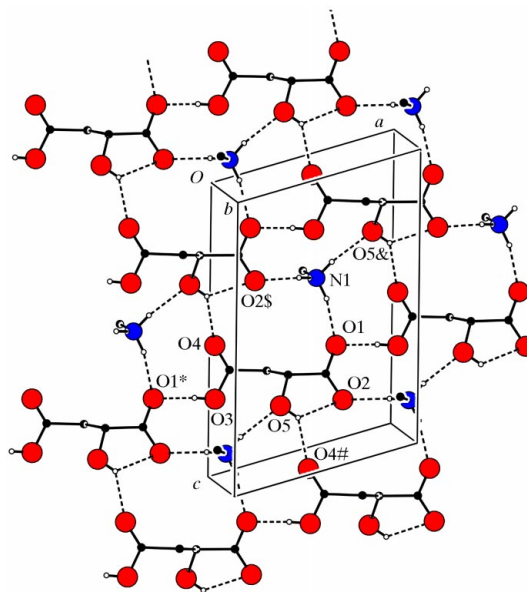


Figure 5

Part of the crystal structure of (I), showing the formation of an (010) sheet of anions with cations pendent from it. For the sake of clarity, H atoms bonded to C atoms have been omitted, as have the phenyl and methyl groups in the cation. Atoms marked with an asterisk (*), hash (#), dollar sign (\$) or ampersand (&) are at the symmetry positions $(x - 1, y, z)$, $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, $(x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2})$ and $(\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2})$, respectively.

(II), in compound (III) the remaining carboxyl H in the anion is disordered unequally between the carboxyl atoms O3 and O1, with the corresponding atoms H3 and H1 having site occupancies of 0.87 (4) and 0.13 (4), respectively (Fig. 3). Since the two atoms concerned (O3 adjacent to the major-occupancy site of this disordered H atom and O1 adjacent to the minor-occupancy site) participate in an inter-anion O—H \cdots O hydrogen bond, the H-atom component of this bond is disordered over two sites, but the disorder has no influence on the overall supramolecular structure. The anion in (II) exhibits configurational disorder such that both enantiomers share a common set of sites for all O atoms and for the carboxyl atoms C1 and C4 (Fig. 4).

In each of compounds (I)–(III), there is an intramolecular O—H \cdots O hydrogen bond within the anion (Figs. 1–3) and this probably exercises some influence on the conformation of the anion. The two ions within each asymmetric unit are linked by a single N—H \cdots O hydrogen bond (Tables 1–3).

The anions in (I) form a two-dimensional substructure from which the cations are pendent. Carboxyl atom O3 in the anion at (x, y, z) acts as hydrogen-bond donor to carboxylate atom

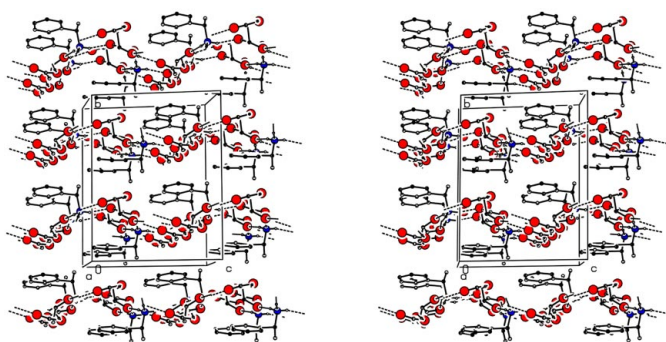


Figure 6
A stereoview of part of the crystal structure of (I), showing the tripartite sandwich structure of the (010) sheets. For the sake of clarity, H atoms bonded to C atoms have been omitted.

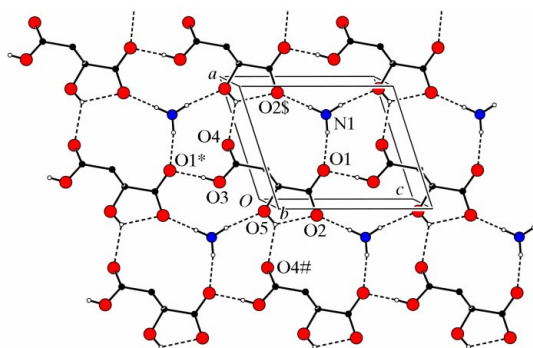


Figure 7
Part of the crystal structure of (III), showing the formation of an (010) sheet of anions with cations pendent from it. For the sake of clarity, only the major component of the disordered hydrogen bond is shown, and H atoms bonded to C atoms, as well as the phenyl and methyl groups, have been omitted. Atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(x, y, z - 1)$, $(x - 1, y, z)$ and $(1 + x, y, z)$, respectively.

O1 in the anion at $(x - 1, y, z)$, so generating by translation a $C(7)$ chain (Bernstein *et al.*, 1995) running parallel to the [100] direction. Four chains of this type pass through each unit cell. In addition, hydroxyl atom O5 in the anion at (x, y, z) acts as hydrogen-bond donor to carboxyl atom O4 in the anion at $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, while atom O5 at $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$ in turn acts as donor to atom O4 at $(1 + x, y, 1 + z)$. Hence, a $C(6)$ chain is produced, running parallel to the [101] direction and generated by the n -glide plane at $y = \frac{1}{4}$. The [100] and [101] chains generate an (010) sheet built from a single type of $R_4^2(22)$ ring (Fig. 5). Two anion sheets pass through each unit cell, lying in the domains $0.13 < y < 0.37$ and $0.63 < y < 0.83$, generated by the n -glide planes at $y = \frac{1}{4}$ and $y = \frac{3}{4}$, respectively.

The cation is linked to the anion sheet by three N—H \cdots O hydrogen bonds (Table 1). Ammonium atom N1 in the cation at (x, y, z) is linked, *via* atoms H1A, H1B and H1C, respectively, to atom O1 in the anion at (x, y, z) , O2 in the anion at $(x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2})$ and O5 in the anion at $(x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2})$, all three of which lie in the same (010) sheet generated by the $y = \frac{1}{4}$ glide plane. The action of this glide plane produces equal numbers of cations on the two faces of the anion sheet, with the R cations all on one face of the anion sheet and the S cations all on the opposite face, and such that the methyl and phenyl components of the cations fill the laminal spaces between the anion sheets (Fig. 6). Hence, each sheet is effectively tripartite in nature, with a polar central layer sandwiched between two lipophilic layers. There are no direction-specific interactions between the lipophilic components of adjacent sheets. In particular, there are neither X —H $\cdots\pi$ (arene) hydrogen bonds (for any of $X = C, N$ or O) nor aromatic π — π stacking interactions.

Although compound (III) crystallizes in a different space group ($P2_1$) from that of (I) (Cc), the anion substructure has a very similar overall topology. Carboxyl atom O3 in the anion at (x, y, z) acts as hydrogen-bond donor to carboxylate atom O1 in the anion at $(x, y, z - 1)$, so generating by translation a $C(7)$ chain running parallel to the [001] direction (Fig. 7) [*cf.* the [100] $C(7)$ chain in compound (I) (Fig. 5)]. Just two chains

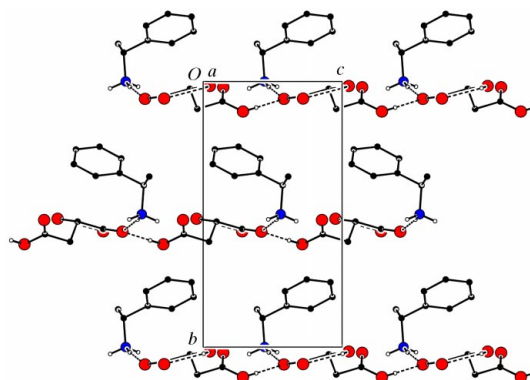


Figure 8
A projection of part of the crystal structure of (III), showing the (010) sheets, with cations pendent from only one face of the anion sheet. For the sake of clarity, only the major component of the disordered hydrogen bond is shown, and H atoms bonded to C atoms have been omitted.

of this type pass through each unit cell. Hydroxyl atom O5 in the anion at (x, y, z) acts as hydrogen-bond donor to carboxyl atom O4 in the anion at $(x - 1, y, z)$, so generating by translation a $C(6)$ chain running parallel to the $[100]$ direction (Fig. 7) [*cf.* the $[101]$ $C(6)$ chain in compound (I) (Fig. 5)]. Again, there are two of these chains per unit cell. The combination of the $[100]$ and $[001]$ chains in (III) produces an (010) sheet, entirely analogous to the sheet in (I), except that the chiral sheet in (III) is generated by translation and contains only a single enantiomer, while that in (I) is generated by a glide plane and so contains both enantiomers of the anion. Two sheets of this type pass through each unit cell in (III), in the domains $0.01 < y < 0.11$ and $0.51 < y < 0.61$, so that these sheets are much thinner than those in compound (I) (Figs. 6 and 8).

The cation in (III) is again linked to the anion sheet by three $N-H \cdots O$ hydrogen bonds (Table 2). Atom N1 in the cation at (x, y, z) acts as hydrogen-bond donor, *via* atoms H1A, H1B and H1C, respectively, to atom O1 in the anion at (x, y, z) , O2 at $(1 + x, y, z)$ and O5 at $(1 + x, y, 1 + z)$, all of which lie in the same (010) sheet (Figs. 7 and 8). Hence, by contrast with (I) (Fig. 6), in (III) there are cations linked to only one face of an anion sheet, and all the cations have the same *R* configuration.

In compound (II) (Fig. 3), the cations all have the *R* configuration, as in (III), but only *ca* 75% of the anion sites are occupied by (*S*)-malate ions and some 25% of these sites are occupied by (*R*)-malate ions. Compound (II) was prepared from racemic malic acid and hence its formation indicates a modest degree of enantioselectivity during the crystallization process, which in turn implies a modest degree of enantioselective recognition. Since the two orientations of the anions share a common set of O-atom sites (Fig. 4), we shall, for the sake of convenience and clarity, discuss primarily the effects of the major (*S*)-enantiomer.

Compounds (II) and (III) both crystallize in space group $P2_1$. Although their cell dimensions are certainly similar, they are by no means identical. The anion substructures are very

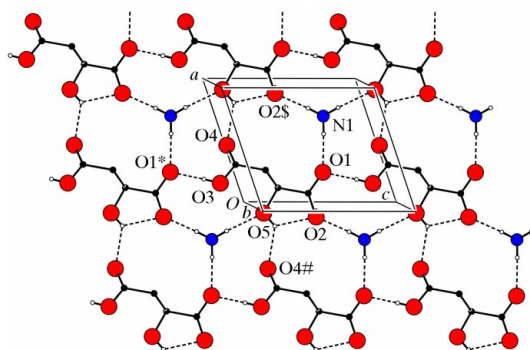


Figure 9

Part of the crystal structure of (II), showing the formation of an (010) sheet of anions with cations pendent from it. For the sake of clarity, only the major component of the disordered anion is shown, and H atoms bonded to C atoms, as well as the phenyl and methyl groups, have been omitted. Atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(x, y, z - 1)$, $(x - 1, y, z)$ and $(1 + x, y, z)$, respectively.

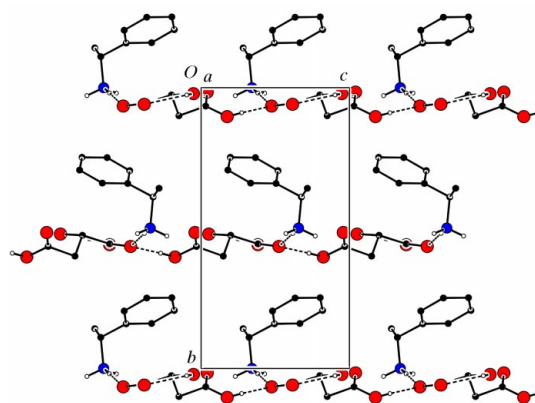


Figure 10

A projection of part of the crystal structure of (II), showing the (010) sheets, with cations pendent from only one face of the anion sheet. For the sake of clarity, only the major component of the disordered anion is shown, and H atoms bonded to C atoms have been omitted.

similar and both are generated by translation (Tables 2 and 3); however, that in (II) is somewhat displaced relative to that in (III). Detailed comparison of the coordinates of corresponding atoms in (II) and (III) shows that, consistently, the x and y coordinates are very similar, but that the z coordinates are all *ca* 0.1 greater in (II) (Figs. 7–10). Successive sheets are related by the 2_1 axis, so that the offset between successive sheets differs by *ca* 0.2*z* or *ca* 1.5 Å between (II) and (III). As in (III), the cations in (II) are pendent from only one face of the anion sheet, and the projections of the two structures (Figs. 8 and 10) clearly show the relative displacement of the sheets in the $[001]$ direction.

We note that, while in (II) crystallization of the (*R*)-amine with the *rac*-acid gives a preponderance of (*S*)-malic acid units in the product, all attempts to obtain good quality crystals of the salts containing two enantiopure *S* components, *i.e.* the enantiomorph of the *R,R* salt, have to date been unsuccessful.

Experimental

For the synthesis of compounds (I)–(V), equimolar quantities of the appropriate isomers of 1-phenylethylamine and malic acid were separately dissolved in methanol. The appropriate pairs of solutions were mixed and the mixtures were then set aside to crystallize, providing analytically pure samples of (I)–(V). Analyses, found for (I): C 56.3, H 6.7, N 5.5%; found for (II): C 56.0, H 6.7, N 5.5%; found for (III): C 56.7, H 6.8, N 5.4%; found for (IV): C 57.0, H 6.7, N 5.4%; found for (V): C 56.4, H 7.5, N 5.5%; $C_{12}H_{17}NO_5$ requires: C 56.5, H 6.7, N 5.5%. For the synthesis of (VI), stoichiometric quantities of racemic 1-phenylethylamine and (*S*)-malic acid (2:1 molar ratio) were separately dissolved in methanol. The solutions were mixed and the mixture was then set aside to crystallize, providing analytically pure (VI). Analysis for (VI), found: C 63.5, H 8.0, N 7.4%; $C_{20}H_{28}N_2O_5$ requires: C 63.8, H 7.5, N 7.4%. Single crystals of compounds (I)–(III) suitable for single-crystal X-ray diffraction were selected directly from the prepared samples. Despite repeated attempts, no suitable crystals of compounds (IV)–(VI) have yet been obtained.

Compound (I)

Crystal data

| | |
|----------------------------------|---|
| $C_8H_{12}N^+ \cdot C_4H_5O_5^-$ | $D_x = 1.340 \text{ Mg m}^{-3}$ |
| $M_r = 255.27$ | Mo $K\alpha$ radiation |
| Monoclinic, Cc | Cell parameters from 13 550 reflections |
| $a = 7.5373 (5) \text{ \AA}$ | $\theta = 2.7\text{--}25.0^\circ$ |
| $b = 15.0354 (15) \text{ \AA}$ | $\mu = 0.11 \text{ mm}^{-1}$ |
| $c = 11.6624 (12) \text{ \AA}$ | $T = 150 (1) \text{ K}$ |
| $\beta = 106.811 (5)^\circ$ | Plate, colourless |
| $V = 1265.2 (2) \text{ \AA}^3$ | $0.34 \times 0.32 \times 0.14 \text{ mm}$ |
| $Z = 4$ | |

Data collection

| | |
|---|------------------------------------|
| Nonius KappaCCD diffractometer | $R_{\text{int}} = 0.134$ |
| φ scans, and ω scans with κ offsets | $\theta_{\text{max}} = 25.0^\circ$ |
| 6949 measured reflections | $h = -8 \rightarrow 8$ |
| 1101 independent reflections | $k = -17 \rightarrow 17$ |
| 1037 reflections with $I > 2\sigma(I)$ | $l = -13 \rightarrow 13$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0795P)^2 + 0.3357P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.045$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.121$ | $(\Delta/\sigma)_{\text{max}} = 0.002$ |
| $S = 1.05$ | $\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$ |
| 1101 reflections | $\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$ |
| 168 parameters | Extinction correction: <i>SHELXL97</i> |
| H-atom parameters constrained | Extinction coefficient: 0.037 (7) |

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$) for (I).

| $D\text{--}H\cdots A$ | $D\text{--}H$ | $H\cdots A$ | $D\cdots A$ | $D\text{--}H\cdots A$ |
|---------------------------------|---------------|-------------|-------------|-----------------------|
| $O3\text{--}H3\cdots O1^i$ | 0.84 | 1.69 | 2.528 (3) | 176 |
| $O5\text{--}H5\cdots O4^{ii}$ | 0.84 | 2.12 | 2.779 (4) | 135 |
| $O5\text{--}H5\cdots O2$ | 0.84 | 2.15 | 2.650 (3) | 118 |
| $N1\text{--}H1A\cdots O1$ | 0.91 | 1.95 | 2.822 (4) | 159 |
| $N1\text{--}H1B\cdots O2^{iii}$ | 0.91 | 1.93 | 2.817 (4) | 163 |
| $N1\text{--}H1C\cdots O5^{iv}$ | 0.91 | 2.02 | 2.917 (4) | 167 |

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

Compound (II)

Crystal data

| | |
|----------------------------------|---|
| $C_8H_{12}N^+ \cdot C_4H_5O_5^-$ | $D_x = 1.360 \text{ Mg m}^{-3}$ |
| $M_r = 255.27$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1$ | Cell parameters from 1482 reflections |
| $a = 6.4227 (5) \text{ \AA}$ | $\theta = 2.9\text{--}27.5^\circ$ |
| $b = 13.5815 (10) \text{ \AA}$ | $\mu = 0.11 \text{ mm}^{-1}$ |
| $c = 7.5439 (3) \text{ \AA}$ | $T = 150 (1) \text{ K}$ |
| $\beta = 108.665 (4)^\circ$ | Needle, colourless |
| $V = 623.44 (7) \text{ \AA}^3$ | $0.32 \times 0.14 \times 0.12 \text{ mm}$ |
| $Z = 2$ | |

Data collection

| | |
|---|------------------------------------|
| Nonius KappaCCD diffractometer | $R_{\text{int}} = 0.064$ |
| φ scans, and ω scans with κ offsets | $\theta_{\text{max}} = 27.4^\circ$ |
| 5426 measured reflections | $h = -8 \rightarrow 7$ |
| 1482 independent reflections | $k = -16 \rightarrow 17$ |
| 1391 reflections with $I > 2\sigma(I)$ | $l = -9 \rightarrow 9$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 0.0754P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.094$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| $S = 1.04$ | $\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$ |
| 1482 reflections | $\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$ |
| 176 parameters | Extinction correction: <i>SHELXL97</i> |
| H-atom parameters constrained | Extinction coefficient: 0.22 (3) |

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$) for (II).

| $D\text{--}H\cdots A$ | $D\text{--}H$ | $H\cdots A$ | $D\cdots A$ | $D\text{--}H\cdots A$ |
|---------------------------------|---------------|-------------|-------------|-----------------------|
| $O3\text{--}H3\cdots O1^i$ | 0.84 | 1.71 | 2.546 (2) | 178 |
| $O5\text{--}H5\cdots O2$ | 0.84 | 2.11 | 2.615 (2) | 119 |
| $O5\text{--}H5\cdots O4^{ii}$ | 0.84 | 2.14 | 2.755 (2) | 129 |
| $N1\text{--}H1A\cdots O1$ | 0.91 | 1.97 | 2.882 (2) | 177 |
| $N1\text{--}H1B\cdots O2^{iii}$ | 0.91 | 1.91 | 2.815 (2) | 177 |
| $N1\text{--}H1C\cdots O5^{iv}$ | 0.91 | 2.03 | 2.869 (2) | 152 |

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

Compound (III)

Crystal data

| | |
|----------------------------------|---|
| $C_8H_{12}N^+ \cdot C_4H_5O_5^-$ | Mo $K\alpha$ radiation |
| $M_r = 255.27$ | Cell parameters from 1504 reflections |
| Monoclinic, $P2_1$ | $\theta = 2.8\text{--}27.5^\circ$ |
| $a = 6.3350 (2) \text{ \AA}$ | $\mu = 0.11 \text{ mm}^{-1}$ |
| $b = 13.7876 (6) \text{ \AA}$ | $T = 150 (1) \text{ K}$ |
| $c = 7.5572 (2) \text{ \AA}$ | Block, colourless |
| $\beta = 107.907 (2)^\circ$ | $0.26 \times 0.20 \times 0.18 \text{ mm}$ |
| $V = 628.10 (4) \text{ \AA}^3$ | |
| $Z = 2$ | |
| $D_x = 1.350 \text{ Mg m}^{-3}$ | |

Data collection

| | |
|---|------------------------------------|
| Nonius KappaCCD diffractometer | $R_{\text{int}} = 0.066$ |
| φ scans, and ω scans with κ offsets | $\theta_{\text{max}} = 27.5^\circ$ |
| 5348 measured reflections | $h = -8 \rightarrow 7$ |
| 1504 independent reflections | $k = -17 \rightarrow 18$ |
| 1398 reflections with $I > 2\sigma(I)$ | $l = -9 \rightarrow 9$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.0897P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.032$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.078$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| $S = 1.06$ | $\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$ |
| 1504 reflections | $\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$ |
| 170 parameters | Extinction correction: <i>SHELXL97</i> |
| H-atom parameters constrained | Extinction coefficient: 0.042 (12) |

Table 3

Hydrogen-bonding geometry (\AA , $^\circ$) for (III).

| $D\text{--}H\cdots A$ | $D\text{--}H$ | $H\cdots A$ | $D\cdots A$ | $D\text{--}H\cdots A$ |
|--------------------------------|---------------|-------------|-------------|-----------------------|
| $O1\text{--}H1\cdots O3^i$ | 0.84 | 1.73 | 2.548 (2) | 164 |
| $O3\text{--}H3\cdots O1^{ii}$ | 0.84 | 1.71 | 2.548 (2) | 176 |
| $O5\text{--}H5\cdots O2$ | 0.84 | 2.13 | 2.629 (2) | 118 |
| $O5\text{--}H5\cdots O4^{iii}$ | 0.84 | 2.17 | 2.777 (2) | 129 |
| $N1\text{--}H1A\cdots O1$ | 0.91 | 1.96 | 2.865 (2) | 170 |
| $N1\text{--}H1B\cdots O2^{iv}$ | 0.91 | 1.92 | 2.834 (2) | 178 |
| $N1\text{--}H1C\cdots O5^v$ | 0.91 | 2.05 | 2.877 (2) | 151 |

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

For compound (I), the systematic absences permitted Cc and $C2/c$ as possible space groups. Cc was selected and confirmed by the subsequent analysis. For each of (II) and (III), the systematic absences permitted $P2_1$ and $P2_1/m$ as possible space groups. In each case, $P2_1$ was selected and confirmed by the subsequent analysis. In compound (II), the anion was found to be disordered over two orientations, such that all of the O-atom sites and the sites for atoms C1 and C4 were common to both orientations, but with distinct sites for atoms C2 and C3 and their associated H atoms, leading to different stereochemical configurations for the two orientations. The site occupancies for the major S and minor R configurations

refined to 0.745 (8) and 0.255 (8), respectively. All H atoms were located from difference maps and subsequently treated as riding atoms, with C—H distances of 0.95 (aromatic), 0.98 (CH₃), 0.99 (CH₂) or 1.00 Å (aliphatic CH), N—H distances of 0.91 Å and O—H distances of 0.84 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, or $1.5U_{\text{eq}}(\text{C})$ for the methyl groups, and $1.5U_{\text{eq}}(\text{N},\text{O})$. All H atoms were fully ordered with respect to their parent atoms, except for the residual carboxyl H atom in (III), which was found to be disordered over two sites, one denoted H3 adjacent to O3 and the other denoted H1 adjacent to O1, with occupancies 0.87 (4) and 0.13 (4), respectively. In order to ensure maximum comparability of the structures of (II) and (III), the y coordinate of atom N1 in each was initially fixed at 0.5 and only allowed to refine in the final cycles. In the absence of significant anomalous scattering, the values of the Flack (1983) parameter were indeterminate (Flack & Bernardinelli, 2000). Accordingly, the Friedel-equivalent reflections were merged prior to the final refinements. It was therefore not possible to establish the correct orientation of the structure of (I) relative to the polar-axis directions (Jones, 1986). For both (II) and (III), the correct enantiomorph was selected by reference to the known absolute configuration of the enantiopure amine component.

For all three compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); 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, 2003); software used to prepare material for publication: *SHELXL97* 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: SK1743). Services for accessing these data are described at the back of the journal.

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supporting information

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Supramolecular structures of three configurational isomers of 1-phenylethanaminium malate(1–)

David E. Turkington, George Ferguson, Alan J. Lough and Christopher Glidewell

Computing details

For all compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); 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, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

(I) rac-1-phenylethanaminium rac-malate(1–)

Crystal data

$C_8H_{12}N^+ \cdot C_4H_5O_5^-$

$M_r = 255.27$

Monoclinic, *Cc*

Hall symbol: C -2yc

$a = 7.5373$ (5) Å

$b = 15.0354$ (15) Å

$c = 11.6624$ (12) Å

$\beta = 106.811$ (5)°

$V = 1265.2$ (2) Å³

$Z = 4$

$F(000) = 544$

$D_x = 1.340$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 13550 reflections

$\theta = 2.7$ – 25.0°

$\mu = 0.11$ mm⁻¹

$T = 150$ K

Plate, colourless

$0.34 \times 0.32 \times 0.14$ mm

Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed X-ray tube

Graphite monochromator

φ scans, and ω scans with κ offsets

6949 measured reflections

1101 independent reflections

1037 reflections with $I > 2\sigma(I)$

$R_{int} = 0.134$

$\theta_{max} = 25.0^\circ$, $\theta_{min} = 2.7^\circ$

$h = -8 \rightarrow 8$

$k = -17 \rightarrow 17$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.121$

$S = 1.05$

1101 reflections

168 parameters

2 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0795P)^2 + 0.3357P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.18$ e Å⁻³

$\Delta\rho_{min} = -0.27$ e Å⁻³

Extinction correction: *SHELXL97* (Sheldrick, 1997), $F_c^* = kFc[1 + 0.001xFe^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.037 (7)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{iso}^*/U_{eq} |
|------|-------------|--------------|------------|--------------------|
| O1 | 0.6694 (3) | 0.17654 (18) | 0.6623 (2) | 0.0444 (6) |
| O2 | 0.7039 (3) | 0.21943 (19) | 0.8514 (2) | 0.0433 (6) |
| O3 | 0.0126 (3) | 0.1428 (2) | 0.7286 (2) | 0.0469 (7) |
| O4 | 0.0035 (4) | 0.1775 (2) | 0.5422 (2) | 0.0538 (7) |
| O5 | 0.3542 (3) | 0.27134 (19) | 0.8048 (2) | 0.0454 (6) |
| C1 | 0.6102 (4) | 0.2054 (3) | 0.7465 (3) | 0.0404 (8) |
| C2 | 0.4005 (5) | 0.2256 (3) | 0.7106 (3) | 0.0420 (8) |
| C3 | 0.2963 (4) | 0.1380 (3) | 0.6839 (3) | 0.0435 (8) |
| C4 | 0.0890 (4) | 0.1546 (2) | 0.6426 (3) | 0.0402 (8) |
| N1 | 0.5537 (4) | 0.19757 (19) | 0.4111 (2) | 0.0383 (7) |
| C11 | 0.3667 (5) | 0.0979 (2) | 0.2540 (3) | 0.0429 (8) |
| C12 | 0.4316 (6) | 0.1122 (3) | 0.1562 (4) | 0.0569 (11) |
| C13 | 0.3055 (10) | 0.1059 (4) | 0.0391 (4) | 0.0802 (18) |
| C14 | 0.1203 (9) | 0.0858 (3) | 0.0257 (5) | 0.0772 (17) |
| C15 | 0.0605 (7) | 0.0731 (3) | 0.1204 (5) | 0.0683 (14) |
| C16 | 0.1805 (5) | 0.0786 (3) | 0.2347 (4) | 0.0509 (9) |
| C17 | 0.4927 (5) | 0.1032 (2) | 0.3817 (3) | 0.0438 (8) |
| C18 | 0.6590 (6) | 0.0423 (3) | 0.4069 (4) | 0.0633 (13) |
| H3 | −0.1013 | 0.1540 | 0.7030 | 0.070* |
| H5 | 0.4502 | 0.2786 | 0.8624 | 0.068* |
| H2 | 0.3670 | 0.2634 | 0.6369 | 0.050* |
| H3A | 0.3340 | 0.1057 | 0.6207 | 0.052* |
| H3B | 0.3279 | 0.1006 | 0.7568 | 0.052* |
| H1C | 0.6350 | 0.2132 | 0.3701 | 0.057* |
| H1A | 0.6099 | 0.2026 | 0.4911 | 0.057* |
| H1B | 0.4533 | 0.2342 | 0.3898 | 0.057* |
| H12 | 0.5584 | 0.1261 | 0.1670 | 0.068* |
| H13 | 0.3474 | 0.1153 | −0.0294 | 0.096* |
| H14 | 0.0360 | 0.0812 | −0.0524 | 0.093* |
| H15 | −0.0666 | 0.0600 | 0.1096 | 0.082* |
| H16 | 0.1346 | 0.0691 | 0.3015 | 0.061* |
| H17 | 0.4180 | 0.0853 | 0.4361 | 0.053* |
| H18A | 0.7349 | 0.0501 | 0.4900 | 0.095* |
| H18B | 0.7330 | 0.0569 | 0.3527 | 0.095* |
| H18C | 0.6171 | −0.0196 | 0.3942 | 0.095* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|-------------|--------------|-------------|--------------|
| O1 | 0.0270 (11) | 0.0690 (16) | 0.0360 (13) | 0.0013 (11) | 0.0071 (10) | −0.0042 (11) |
| O2 | 0.0301 (11) | 0.0632 (17) | 0.0338 (12) | −0.0023 (10) | 0.0051 (9) | −0.0038 (11) |
| O3 | 0.0283 (11) | 0.0734 (19) | 0.0360 (13) | 0.0056 (11) | 0.0046 (10) | −0.0019 (11) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| O4 | 0.0424 (14) | 0.0760 (19) | 0.0419 (16) | -0.0072 (12) | 0.0101 (12) | 0.0090 (13) |
| O5 | 0.0281 (11) | 0.0595 (15) | 0.0466 (15) | -0.0013 (11) | 0.0076 (10) | -0.0132 (12) |
| C1 | 0.0284 (16) | 0.053 (2) | 0.0380 (19) | -0.0030 (14) | 0.0066 (14) | -0.0051 (15) |
| C2 | 0.0277 (15) | 0.056 (2) | 0.0407 (19) | -0.0018 (15) | 0.0075 (13) | -0.0084 (16) |
| C3 | 0.0311 (17) | 0.052 (2) | 0.045 (2) | -0.0023 (15) | 0.0069 (14) | -0.0061 (16) |
| C4 | 0.0317 (16) | 0.0510 (19) | 0.037 (2) | -0.0059 (14) | 0.0079 (15) | -0.0064 (15) |
| N1 | 0.0316 (13) | 0.0464 (16) | 0.0331 (15) | -0.0002 (12) | 0.0033 (11) | 0.0003 (12) |
| C11 | 0.0471 (19) | 0.0407 (19) | 0.0328 (18) | 0.0001 (15) | -0.0012 (14) | 0.0000 (14) |
| C12 | 0.069 (3) | 0.055 (2) | 0.045 (2) | -0.0048 (19) | 0.014 (2) | 0.0014 (17) |
| C13 | 0.147 (6) | 0.055 (3) | 0.041 (3) | 0.004 (3) | 0.030 (3) | 0.0003 (19) |
| C14 | 0.093 (4) | 0.052 (3) | 0.058 (3) | 0.001 (3) | -0.024 (3) | -0.006 (2) |
| C15 | 0.064 (3) | 0.052 (3) | 0.068 (3) | 0.003 (2) | -0.015 (2) | -0.005 (2) |
| C16 | 0.043 (2) | 0.046 (2) | 0.054 (2) | -0.0016 (16) | -0.0020 (16) | -0.0073 (17) |
| C17 | 0.0379 (17) | 0.049 (2) | 0.0371 (19) | -0.0022 (15) | -0.0012 (14) | 0.0034 (15) |
| C18 | 0.049 (2) | 0.049 (2) | 0.073 (3) | 0.0011 (17) | -0.013 (2) | -0.002 (2) |

Geometric parameters (Å, °)

| | | | |
|----------|-----------|-------------|-----------|
| O1—C1 | 1.267 (4) | C11—C12 | 1.382 (5) |
| O2—C1 | 1.241 (4) | C11—C16 | 1.386 (5) |
| O3—C4 | 1.305 (4) | C11—C17 | 1.519 (5) |
| O3—H3 | 0.84 | C12—C13 | 1.424 (7) |
| O4—C4 | 1.212 (4) | C12—H12 | 0.95 |
| O5—C2 | 1.423 (4) | C13—C14 | 1.392 (9) |
| O5—H5 | 0.84 | C13—H13 | 0.95 |
| C1—C2 | 1.544 (4) | C14—C15 | 1.322 (8) |
| C2—C3 | 1.518 (5) | C14—H14 | 0.95 |
| C2—H2 | 1.00 | C15—C16 | 1.380 (6) |
| C3—C4 | 1.517 (4) | C15—H15 | 0.95 |
| C3—H3A | 0.99 | C16—H16 | 0.95 |
| C3—H3B | 0.99 | C17—C18 | 1.512 (6) |
| N1—C17 | 1.500 (5) | C17—H17 | 1.00 |
| N1—H1C | 0.91 | C18—H18A | 0.98 |
| N1—H1A | 0.91 | C18—H18B | 0.98 |
| N1—H1B | 0.91 | C18—H18C | 0.98 |
| C4—O3—H3 | 109.5 | C16—C11—C17 | 119.1 (3) |
| C2—O5—H5 | 109.5 | C11—C12—C13 | 118.9 (4) |
| O2—C1—O1 | 126.5 (3) | C11—C12—H12 | 120.5 |
| O2—C1—C2 | 118.7 (3) | C13—C12—H12 | 120.5 |
| O1—C1—C2 | 114.7 (3) | C14—C13—C12 | 119.4 (4) |
| O5—C2—C3 | 110.5 (3) | C14—C13—H13 | 120.3 |
| O5—C2—C1 | 110.2 (3) | C12—C13—H13 | 120.3 |
| C3—C2—C1 | 108.3 (3) | C15—C14—C13 | 120.7 (4) |
| O5—C2—H2 | 109.3 | C15—C14—H14 | 119.6 |
| C3—C2—H2 | 109.3 | C13—C14—H14 | 119.6 |
| C1—C2—H2 | 109.3 | C14—C15—C16 | 120.8 (5) |
| C4—C3—C2 | 110.3 (3) | C14—C15—H15 | 119.6 |

| | | | |
|-----------------|------------|-----------------|------------|
| C4—C3—H3A | 109.6 | C16—C15—H15 | 119.6 |
| C2—C3—H3A | 109.6 | C15—C16—C11 | 121.3 (4) |
| C4—C3—H3B | 109.6 | C15—C16—H16 | 119.4 |
| C2—C3—H3B | 109.6 | C11—C16—H16 | 119.4 |
| H3A—C3—H3B | 108.1 | N1—C17—C18 | 110.3 (3) |
| O4—C4—O3 | 123.5 (3) | N1—C17—C11 | 109.7 (3) |
| O4—C4—C3 | 124.4 (3) | C18—C17—C11 | 114.0 (3) |
| O3—C4—C3 | 112.2 (3) | N1—C17—H17 | 107.5 |
| C17—N1—H1C | 109.5 | C18—C17—H17 | 107.5 |
| C17—N1—H1A | 109.5 | C11—C17—H17 | 107.5 |
| H1C—N1—H1A | 109.5 | C17—C18—H18A | 109.5 |
| C17—N1—H1B | 109.5 | C17—C18—H18B | 109.5 |
| H1C—N1—H1B | 109.5 | H18A—C18—H18B | 109.5 |
| H1A—N1—H1B | 109.5 | C17—C18—H18C | 109.5 |
| C12—C11—C16 | 118.9 (4) | H18A—C18—H18C | 109.5 |
| C12—C11—C17 | 122.0 (3) | H18B—C18—H18C | 109.5 |
| O2—C1—C2—O5 | 8.9 (5) | C11—C12—C13—C14 | 0.2 (7) |
| O1—C1—C2—O5 | -170.1 (3) | C12—C13—C14—C15 | 0.4 (7) |
| O2—C1—C2—C3 | -112.0 (4) | C13—C14—C15—C16 | -0.6 (7) |
| O1—C1—C2—C3 | 68.9 (4) | C14—C15—C16—C11 | 0.2 (7) |
| O5—C2—C3—C4 | 61.7 (4) | C12—C11—C16—C15 | 0.4 (6) |
| C1—C2—C3—C4 | -177.5 (3) | C17—C11—C16—C15 | 180.0 (4) |
| C2—C3—C4—O4 | 79.2 (5) | C12—C11—C17—N1 | 68.2 (4) |
| C2—C3—C4—O3 | -99.7 (4) | C16—C11—C17—N1 | -111.4 (4) |
| C16—C11—C12—C13 | -0.6 (6) | C12—C11—C17—C18 | -56.0 (5) |
| C17—C11—C12—C13 | 179.8 (4) | C16—C11—C17—C18 | 124.4 (4) |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| O3—H3...O1 ⁱ | 0.84 | 1.69 | 2.528 (3) | 176 |
| O5—H5...O4 ⁱⁱ | 0.84 | 2.12 | 2.779 (4) | 135 |
| O5—H5...O2 | 0.84 | 2.15 | 2.650 (3) | 118 |
| N1—H1A...O1 | 0.91 | 1.95 | 2.822 (4) | 159 |
| N1—H1B...O2 ⁱⁱⁱ | 0.91 | 1.93 | 2.817 (4) | 163 |
| N1—H1C...O5 ^{iv} | 0.91 | 2.02 | 2.917 (4) | 167 |

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

(II) (R)-1-phenylethanaminium (S)-malate(1-)

Crystal data

$C_8H_{12}N^+ \cdot C_4H_5O_5^-$
 $M_r = 255.27$
 Monoclinic, $P2_1$
 Hall symbol: P 2yb
 $a = 6.4227$ (5) Å
 $b = 13.5815$ (10) Å
 $c = 7.5439$ (3) Å

$\beta = 108.665$ (4)°
 $V = 623.44$ (7) Å³
 $Z = 2$
 $F(000) = 272$
 $D_x = 1.360$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 1482 reflections

$\theta = 2.9\text{--}27.5^\circ$
 $\mu = 0.11\text{ mm}^{-1}$
 $T = 150\text{ K}$

Needle, colourless
 $0.32 \times 0.14 \times 0.12\text{ mm}$

Data collection

Nonius KappaCCD
 diffractometer
 Radiation source: fine-focus sealed X-ray tube
 Graphite monochromator
 φ scans, and ω scans with κ offsets
 5426 measured reflections
 1482 independent reflections

1391 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.064$
 $\theta_{\text{max}} = 27.4^\circ$, $\theta_{\text{min}} = 2.9^\circ$
 $h = -8 \rightarrow 7$
 $k = -16 \rightarrow 17$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.094$
 $S = 1.04$
 1482 reflections
 176 parameters
 5 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 0.0754P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.18\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.16\text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 1997), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.22 (3)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|-------------|--------------|--------------|----------------------------------|-----------|
| O1 | 0.2835 (2) | 0.56554 (15) | 0.52472 (19) | 0.0384 (4) | |
| O2 | -0.0794 (2) | 0.55913 (14) | 0.3834 (2) | 0.0396 (4) | |
| O3 | 0.1967 (3) | 0.60310 (14) | -0.1758 (2) | 0.0418 (4) | |
| O4 | 0.4973 (3) | 0.51581 (17) | -0.0412 (2) | 0.0507 (5) | |
| O5 | -0.0516 (3) | 0.52137 (15) | 0.0518 (2) | 0.0442 (5) | |
| C1 | 0.1127 (3) | 0.55626 (19) | 0.3832 (3) | 0.0364 (5) | |
| C2 | 0.1540 (4) | 0.5258 (3) | 0.1998 (4) | 0.0318 (8) | 0.745 (8) |
| C3 | 0.3035 (5) | 0.6000 (3) | 0.1495 (4) | 0.0342 (9) | 0.745 (8) |
| C4 | 0.3444 (4) | 0.5657 (2) | -0.0313 (3) | 0.0445 (6) | |
| C21 | 0.1191 (12) | 0.5796 (8) | 0.1802 (9) | 0.035 (2)* | 0.255 (8) |
| C31 | 0.3321 (13) | 0.5373 (8) | 0.1634 (10) | 0.035 (2)* | 0.255 (8) |
| N1 | 0.7339 (3) | 0.50000 (14) | 0.6569 (2) | 0.0311 (4) | |
| C11 | 0.5908 (4) | 0.34122 (16) | 0.5052 (3) | 0.0340 (5) | |
| C12 | 0.6286 (4) | 0.3399 (2) | 0.3339 (3) | 0.0444 (6) | |
| C13 | 0.4807 (5) | 0.2935 (2) | 0.1808 (4) | 0.0534 (7) | |
| C14 | 0.2954 (5) | 0.24796 (19) | 0.1973 (4) | 0.0546 (7) | |
| C15 | 0.2561 (5) | 0.2491 (2) | 0.3663 (5) | 0.0529 (7) | |
| C16 | 0.4027 (4) | 0.29537 (18) | 0.5185 (4) | 0.0412 (5) | |
| C17 | 0.7470 (4) | 0.38941 (17) | 0.6764 (3) | 0.0336 (5) | |
| C18 | 0.9852 (4) | 0.35830 (18) | 0.7166 (4) | 0.0424 (5) | |
| H3 | 0.2278 | 0.5895 | -0.2730 | 0.063* | |

| | | | | | |
|------|---------|--------|--------|--------|-----------|
| H5 | -0.1551 | 0.5259 | 0.0968 | 0.066* | |
| H2A | 0.2250 | 0.4594 | 0.2165 | 0.038* | 0.745 (8) |
| H3A | 0.4448 | 0.6048 | 0.2525 | 0.041* | 0.745 (8) |
| H3B | 0.2335 | 0.6658 | 0.1304 | 0.041* | 0.745 (8) |
| H21 | 0.1027 | 0.6515 | 0.1504 | 0.042* | 0.255 (8) |
| H31A | 0.3335 | 0.4648 | 0.1769 | 0.042* | 0.255 (8) |
| H31B | 0.4599 | 0.5647 | 0.2628 | 0.042* | 0.255 (8) |
| H1A | 0.5905 | 0.5190 | 0.6179 | 0.047* | |
| H1B | 0.7986 | 0.5194 | 0.5715 | 0.047* | |
| H1C | 0.8047 | 0.5283 | 0.7695 | 0.047* | |
| H12 | 0.7560 | 0.3707 | 0.3214 | 0.053* | |
| H13 | 0.5071 | 0.2932 | 0.0639 | 0.064* | |
| H14 | 0.1955 | 0.2159 | 0.0924 | 0.065* | |
| H15 | 0.1285 | 0.2183 | 0.3781 | 0.063* | |
| H16 | 0.3745 | 0.2958 | 0.6347 | 0.049* | |
| H17 | 0.7010 | 0.3708 | 0.7867 | 0.040* | |
| H18A | 1.0755 | 0.3874 | 0.8352 | 0.064* | |
| H18B | 1.0380 | 0.3811 | 0.6153 | 0.064* | |
| H18C | 0.9957 | 0.2864 | 0.7252 | 0.064* | |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| O1 | 0.0317 (7) | 0.0544 (9) | 0.0305 (7) | 0.0006 (7) | 0.0118 (6) | -0.0026 (7) |
| O2 | 0.0323 (7) | 0.0563 (11) | 0.0318 (7) | 0.0014 (8) | 0.0126 (6) | -0.0007 (7) |
| O3 | 0.0392 (8) | 0.0571 (10) | 0.0338 (8) | 0.0036 (7) | 0.0184 (7) | -0.0037 (7) |
| O4 | 0.0364 (8) | 0.0753 (13) | 0.0399 (9) | 0.0046 (9) | 0.0116 (7) | 0.0115 (8) |
| O5 | 0.0310 (7) | 0.0713 (12) | 0.0313 (7) | -0.0106 (8) | 0.0113 (6) | -0.0063 (7) |
| C1 | 0.0351 (10) | 0.0470 (13) | 0.0288 (9) | -0.0030 (10) | 0.0127 (8) | -0.0010 (9) |
| C2 | 0.0291 (14) | 0.0396 (19) | 0.0279 (13) | -0.0019 (12) | 0.0108 (11) | -0.0024 (11) |
| C3 | 0.0350 (15) | 0.0414 (19) | 0.0282 (14) | -0.0043 (13) | 0.0129 (11) | -0.0039 (11) |
| C4 | 0.0304 (10) | 0.0739 (16) | 0.0313 (10) | -0.0090 (12) | 0.0128 (8) | -0.0014 (11) |
| C1A | 0.0351 (10) | 0.0470 (13) | 0.0288 (9) | -0.0030 (10) | 0.0127 (8) | -0.0010 (9) |
| C4A | 0.0304 (10) | 0.0739 (16) | 0.0313 (10) | -0.0090 (12) | 0.0128 (8) | -0.0014 (11) |
| O5A | 0.0310 (7) | 0.0713 (12) | 0.0313 (7) | -0.0106 (8) | 0.0113 (6) | -0.0063 (7) |
| N1 | 0.0297 (8) | 0.0345 (9) | 0.0309 (8) | 0.0016 (7) | 0.0124 (7) | -0.0017 (7) |
| C11 | 0.0321 (10) | 0.0325 (10) | 0.0366 (10) | 0.0009 (9) | 0.0101 (9) | -0.0012 (8) |
| C12 | 0.0486 (13) | 0.0490 (13) | 0.0371 (12) | -0.0040 (11) | 0.0157 (10) | -0.0045 (10) |
| C13 | 0.0707 (18) | 0.0464 (14) | 0.0378 (12) | 0.0014 (13) | 0.0099 (12) | -0.0083 (11) |
| C14 | 0.0558 (15) | 0.0326 (12) | 0.0575 (17) | -0.0004 (11) | -0.0068 (12) | -0.0069 (11) |
| C15 | 0.0419 (13) | 0.0362 (13) | 0.0719 (19) | -0.0038 (10) | 0.0061 (12) | -0.0017 (12) |
| C16 | 0.0363 (11) | 0.0344 (12) | 0.0531 (13) | -0.0005 (9) | 0.0147 (10) | 0.0004 (10) |
| C17 | 0.0338 (10) | 0.0349 (11) | 0.0327 (10) | -0.0007 (9) | 0.0114 (9) | 0.0022 (8) |
| C18 | 0.0360 (11) | 0.0406 (12) | 0.0474 (13) | 0.0059 (9) | 0.0090 (10) | 0.0008 (10) |

Geometric parameters (Å, °)

| | | | |
|---------------|-------------|---------------|-------------|
| O1—C1 | 1.269 (2) | N1—H1B | 0.91 |
| O2—C1 | 1.235 (3) | N1—H1C | 0.91 |
| O3—C4 | 1.298 (3) | C11—C12 | 1.390 (3) |
| O3—H3 | 0.84 | C11—C16 | 1.391 (3) |
| O4—C4 | 1.215 (3) | C11—C17 | 1.508 (3) |
| O5—C2 | 1.432 (3) | C12—C13 | 1.389 (4) |
| O5—H5 | 0.84 | C12—H12 | 0.95 |
| C1—C2 | 1.547 (3) | C14—C15 | 1.376 (4) |
| C2—C3 | 1.521 (4) | C14—C13 | 1.382 (4) |
| C2—H2A | 1.00 | C14—H14 | 0.95 |
| C3—C4 | 1.541 (3) | C13—H13 | 0.95 |
| C3—H3A | 0.99 | C15—C16 | 1.381 (4) |
| C3—H3B | 0.99 | C15—H15 | 0.95 |
| C21—C31 | 1.526 (9) | C16—H16 | 0.95 |
| C21—H21 | 1.00 | C17—C18 | 1.522 (3) |
| C31—H31A | 0.99 | C17—H17 | 1.00 |
| C31—H31B | 0.99 | C18—H18A | 0.98 |
| N1—C17 | 1.509 (3) | C18—H18B | 0.98 |
| N1—H1A | 0.91 | C18—H18C | 0.98 |
| | | | |
| O2—C1—O1 | 126.25 (18) | C12—C11—C17 | 122.4 (2) |
| O2—C1—C2 | 117.85 (19) | C16—C11—C17 | 119.21 (19) |
| O1—C1—C2 | 115.44 (18) | C13—C12—C11 | 120.1 (2) |
| O5—C2—C3 | 109.4 (2) | C13—C12—H12 | 119.9 |
| O5—C2—C1 | 109.2 (2) | C11—C12—H12 | 119.9 |
| C3—C2—C1 | 110.4 (2) | C15—C14—C13 | 119.8 (2) |
| O5—C2—H2A | 109.3 | C15—C14—H14 | 120.1 |
| C3—C2—H2A | 109.3 | C13—C14—H14 | 120.1 |
| C1—C2—H2A | 109.3 | C14—C13—C12 | 120.5 (2) |
| C2—C3—C4 | 108.7 (2) | C14—C13—H13 | 119.7 |
| C2—C3—H3A | 110.0 | C12—C13—H13 | 119.7 |
| C4—C3—H3A | 110.0 | C14—C15—C16 | 119.8 (3) |
| C2—C3—H3B | 110.0 | C14—C15—H15 | 120.1 |
| C4—C3—H3B | 110.0 | C16—C15—H15 | 120.1 |
| H3A—C3—H3B | 108.3 | C15—C16—C11 | 121.4 (2) |
| O4—C4—O3 | 123.7 (2) | C15—C16—H16 | 119.3 |
| O4—C4—C3 | 126.4 (2) | C11—C16—H16 | 119.3 |
| O3—C4—C3 | 109.8 (2) | C11—C17—N1 | 110.34 (18) |
| C31—C21—H21 | 112.4 | C11—C17—C18 | 113.67 (19) |
| C21—C31—H31A | 110.1 | N1—C17—C18 | 108.49 (18) |
| C21—C31—H31B | 110.1 | C11—C17—H17 | 108.1 |
| H31A—C31—H31B | 108.5 | N1—C17—H17 | 108.1 |
| C17—N1—H1A | 109.5 | C18—C17—H17 | 108.1 |
| C17—N1—H1B | 109.5 | C17—C18—H18A | 109.5 |
| H1A—N1—H1B | 109.5 | C17—C18—H18B | 109.5 |
| C17—N1—H1C | 109.5 | H18A—C18—H18B | 109.5 |

| | | | |
|-----------------|------------|-----------------|------------|
| H1A—N1—H1C | 109.5 | C17—C18—H18C | 109.5 |
| H1B—N1—H1C | 109.5 | H18A—C18—H18C | 109.5 |
| C12—C11—C16 | 118.4 (2) | H18B—C18—H18C | 109.5 |
| O2—C1—C2—O5 | 9.2 (4) | C15—C14—C13—C12 | 0.6 (4) |
| O1—C1—C2—O5 | -178.1 (2) | C11—C12—C13—C14 | -0.4 (4) |
| O2—C1—C2—C3 | 129.5 (3) | C13—C14—C15—C16 | -0.4 (4) |
| O1—C1—C2—C3 | -57.9 (3) | C14—C15—C16—C11 | 0.0 (4) |
| O5—C2—C3—C4 | -61.0 (3) | C12—C11—C16—C15 | 0.1 (4) |
| C1—C2—C3—C4 | 178.8 (2) | C17—C11—C16—C15 | -179.2 (2) |
| C2—C3—C4—O4 | -93.2 (4) | C12—C11—C17—N1 | 72.2 (3) |
| C2—C3—C4—O3 | 90.6 (3) | C16—C11—C17—N1 | -108.6 (2) |
| C16—C11—C12—C13 | 0.0 (4) | C12—C11—C17—C18 | -50.0 (3) |
| C17—C11—C12—C13 | 179.3 (2) | C16—C11—C17—C18 | 129.3 (2) |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|-------|-------------|-------------|---------------|
| O3—H3 \cdots O1 ⁱ | 0.84 | 1.71 | 2.546 (2) | 178 |
| O5—H5 \cdots O2 | 0.84 | 2.11 | 2.615 (2) | 119 |
| O5—H5 \cdots O4 ⁱⁱ | 0.84 | 2.14 | 2.755 (2) | 129 |
| N1—H1A \cdots O1 | 0.91 | 1.97 | 2.882 (2) | 177 |
| N1—H1B \cdots O2 ⁱⁱⁱ | 0.91 | 1.91 | 2.815 (2) | 177 |
| N1—H1C \cdots O5 ^{iv} | 0.91 | 2.03 | 2.869 (2) | 152 |

Symmetry codes: (i) $x, y, z-1$; (ii) $x-1, y, z$; (iii) $x+1, y, z$; (iv) $x+1, y, z+1$.(III) (*R*)-1-phenylethanaminium (*S*)-malate(1-)

Crystal data

 $C_8H_{12}N^+ \cdot C_4H_5O_5^-$ $M_r = 255.27$ Monoclinic, $P2_1$

Hall symbol: P 2yb

 $a = 6.3350$ (2) \AA $b = 13.7876$ (6) \AA $c = 7.5572$ (2) \AA $\beta = 107.907$ (2) $^\circ$ $V = 628.10$ (4) \AA^3 $Z = 2$ $F(000) = 272$ $D_x = 1.350$ Mg m $^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 1504 reflections

 $\theta = 2.8-27.5^\circ$ $\mu = 0.11$ mm $^{-1}$ $T = 150$ K

Block, colourless

 $0.26 \times 0.20 \times 0.18$ mm

Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed X-ray tube

Graphite monochromator

 φ scans, and ω scans with κ offsets

5348 measured reflections

1504 independent reflections

1398 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.066$ $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.8^\circ$ $h = -8 \rightarrow 7$ $k = -17 \rightarrow 16$ $l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.078$

$S = 1.06$

1504 reflections

170 parameters

1 restraint

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.0897P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXL97* (Sheldrick,
1997), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.042 (12)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|-------------|--------------|---------------|----------------------------------|-----------|
| O1 | 0.2791 (2) | 0.56560 (12) | 0.41885 (18) | 0.0266 (3) | |
| O2 | -0.0872 (2) | 0.56439 (11) | 0.28078 (18) | 0.0257 (3) | |
| O3 | 0.1887 (2) | 0.61312 (11) | -0.28668 (19) | 0.0269 (3) | |
| O4 | 0.4823 (2) | 0.52158 (11) | -0.14464 (19) | 0.0278 (3) | |
| O5 | -0.0580 (2) | 0.51704 (12) | -0.04784 (17) | 0.0263 (3) | |
| C1 | 0.1074 (3) | 0.55516 (14) | 0.2801 (2) | 0.0201 (4) | |
| C2 | 0.1460 (3) | 0.52752 (14) | 0.0962 (2) | 0.0199 (4) | |
| C3 | 0.2915 (3) | 0.60348 (15) | 0.0421 (3) | 0.0233 (4) | |
| C4 | 0.3327 (3) | 0.57550 (14) | -0.1385 (2) | 0.0208 (4) | |
| N1 | 0.7292 (2) | 0.50000 (12) | 0.5580 (2) | 0.0219 (4) | |
| C11 | 0.5824 (3) | 0.34513 (14) | 0.3985 (3) | 0.0231 (4) | |
| C12 | 0.6161 (3) | 0.35574 (15) | 0.2261 (3) | 0.0259 (4) | |
| C13 | 0.4729 (4) | 0.31159 (15) | 0.0691 (3) | 0.0292 (5) | |
| C14 | 0.2978 (4) | 0.25585 (16) | 0.0841 (3) | 0.0330 (5) | |
| C15 | 0.2612 (4) | 0.24555 (16) | 0.2542 (3) | 0.0343 (5) | |
| C16 | 0.4042 (3) | 0.28966 (16) | 0.4105 (3) | 0.0298 (4) | |
| C17 | 0.7371 (3) | 0.39112 (16) | 0.5722 (3) | 0.0253 (4) | |
| C18 | 0.9765 (4) | 0.35799 (17) | 0.6121 (3) | 0.0344 (5) | |
| H1 | 0.2420 | 0.5707 | 0.5160 | 0.040* | 0.13 (4) |
| H3 | 0.2243 | 0.5984 | -0.3815 | 0.040* | 0.87 (4) |
| H5 | -0.1637 | 0.5250 | -0.0041 | 0.039* | |
| H2 | 0.2255 | 0.4639 | 0.1135 | 0.024* | |
| H3A | 0.2173 | 0.6675 | 0.0276 | 0.028* | |
| H3B | 0.4350 | 0.6089 | 0.1420 | 0.028* | |
| H1A | 0.5857 | 0.5203 | 0.5276 | 0.033* | |
| H1B | 0.7889 | 0.5194 | 0.4686 | 0.033* | |
| H1C | 0.8081 | 0.5262 | 0.6692 | 0.033* | |
| H12 | 0.7373 | 0.3933 | 0.2154 | 0.031* | |
| H13 | 0.4956 | 0.3198 | -0.0485 | 0.035* | |
| H14 | 0.2024 | 0.2246 | -0.0228 | 0.040* | |
| H15 | 0.1389 | 0.2085 | 0.2641 | 0.041* | |
| H16 | 0.3798 | 0.2818 | 0.5275 | 0.036* | |

| | | | | |
|------|--------|--------|--------|--------|
| H17 | 0.6862 | 0.3719 | 0.6800 | 0.030* |
| H18A | 1.0308 | 0.3772 | 0.5090 | 0.052* |
| H18B | 0.9841 | 0.2873 | 0.6255 | 0.052* |
| H18C | 1.0686 | 0.3881 | 0.7274 | 0.052* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|
| O1 | 0.0210 (6) | 0.0418 (8) | 0.0163 (6) | 0.0019 (6) | 0.0047 (5) | -0.0015 (6) |
| O2 | 0.0199 (6) | 0.0371 (8) | 0.0210 (6) | 0.0003 (6) | 0.0078 (5) | -0.0001 (6) |
| O3 | 0.0247 (7) | 0.0393 (8) | 0.0171 (6) | 0.0071 (6) | 0.0070 (5) | 0.0014 (6) |
| O4 | 0.0229 (7) | 0.0353 (8) | 0.0262 (7) | 0.0057 (6) | 0.0091 (5) | 0.0023 (6) |
| O5 | 0.0174 (6) | 0.0427 (8) | 0.0183 (6) | -0.0034 (6) | 0.0046 (5) | -0.0053 (6) |
| C1 | 0.0216 (8) | 0.0209 (9) | 0.0182 (8) | 0.0005 (7) | 0.0067 (6) | 0.0016 (7) |
| C2 | 0.0184 (8) | 0.0240 (9) | 0.0170 (8) | -0.0005 (7) | 0.0050 (6) | 0.0001 (7) |
| C3 | 0.0219 (9) | 0.0290 (10) | 0.0192 (9) | -0.0061 (8) | 0.0068 (7) | -0.0026 (8) |
| C4 | 0.0166 (8) | 0.0281 (10) | 0.0183 (8) | -0.0042 (7) | 0.0060 (6) | -0.0005 (7) |
| N1 | 0.0188 (7) | 0.0273 (9) | 0.0197 (7) | -0.0003 (6) | 0.0060 (6) | -0.0030 (6) |
| C11 | 0.0205 (9) | 0.0222 (9) | 0.0253 (9) | 0.0020 (7) | 0.0051 (7) | -0.0008 (8) |
| C12 | 0.0260 (10) | 0.0248 (10) | 0.0261 (10) | -0.0014 (8) | 0.0069 (8) | -0.0018 (8) |
| C13 | 0.0359 (11) | 0.0242 (10) | 0.0262 (10) | 0.0041 (9) | 0.0074 (8) | -0.0021 (8) |
| C14 | 0.0319 (11) | 0.0234 (10) | 0.0361 (12) | 0.0008 (8) | -0.0005 (9) | -0.0045 (8) |
| C15 | 0.0282 (11) | 0.0270 (11) | 0.0442 (13) | -0.0049 (9) | 0.0058 (9) | 0.0010 (9) |
| C16 | 0.0264 (10) | 0.0302 (11) | 0.0346 (11) | -0.0001 (9) | 0.0121 (8) | 0.0015 (9) |
| C17 | 0.0265 (10) | 0.0253 (9) | 0.0236 (10) | -0.0008 (8) | 0.0068 (8) | 0.0017 (8) |
| C18 | 0.0285 (11) | 0.0355 (12) | 0.0332 (11) | 0.0068 (9) | 0.0006 (9) | -0.0015 (9) |

Geometric parameters (Å, °)

| | | | |
|--------|-----------|----------|-----------|
| O1—C1 | 1.266 (2) | C11—C16 | 1.389 (3) |
| O1—H1 | 0.84 | C11—C12 | 1.391 (3) |
| O2—C1 | 1.241 (2) | C11—C17 | 1.515 (3) |
| O3—C4 | 1.314 (2) | C12—C13 | 1.392 (3) |
| O3—H3 | 0.84 | C12—H12 | 0.95 |
| O4—C4 | 1.217 (2) | C13—C14 | 1.382 (3) |
| O5—C2 | 1.418 (2) | C13—H13 | 0.95 |
| O5—H5 | 0.84 | C14—C15 | 1.382 (3) |
| C1—C2 | 1.531 (2) | C14—H14 | 0.95 |
| C2—C3 | 1.532 (3) | C15—C16 | 1.388 (3) |
| C2—H2 | 1.00 | C15—H15 | 0.95 |
| C3—C4 | 1.516 (3) | C16—H16 | 0.95 |
| C3—H3A | 0.99 | C17—C18 | 1.522 (3) |
| C3—H3B | 0.99 | C17—H17 | 1.00 |
| N1—C17 | 1.505 (3) | C18—H18A | 0.98 |
| N1—H1A | 0.91 | C18—H18B | 0.98 |
| N1—H1B | 0.91 | C18—H18C | 0.98 |
| N1—H1C | 0.91 | | |

| | | | |
|-----------------|-------------|-----------------|--------------|
| C1—O1—H1 | 109.5 | C12—C11—C17 | 121.52 (18) |
| C4—O3—H3 | 109.5 | C11—C12—C13 | 120.30 (19) |
| C2—O5—H5 | 109.5 | C11—C12—H12 | 119.9 |
| O2—C1—O1 | 125.94 (17) | C13—C12—H12 | 119.9 |
| O2—C1—C2 | 117.73 (15) | C14—C13—C12 | 120.2 (2) |
| O1—C1—C2 | 116.33 (15) | C14—C13—H13 | 119.9 |
| O5—C2—C1 | 111.08 (14) | C12—C13—H13 | 119.9 |
| O5—C2—C3 | 110.23 (15) | C15—C14—C13 | 120.1 (2) |
| C1—C2—C3 | 110.45 (15) | C15—C14—H14 | 120.0 |
| O5—C2—H2 | 108.3 | C13—C14—H14 | 120.0 |
| C1—C2—H2 | 108.3 | C14—C15—C16 | 119.6 (2) |
| C3—C2—H2 | 108.3 | C14—C15—H15 | 120.2 |
| C4—C3—C2 | 110.53 (16) | C16—C15—H15 | 120.2 |
| C4—C3—H3A | 109.5 | C15—C16—C11 | 121.1 (2) |
| C2—C3—H3A | 109.5 | C15—C16—H16 | 119.5 |
| C4—C3—H3B | 109.5 | C11—C16—H16 | 119.5 |
| C2—C3—H3B | 109.5 | N1—C17—C11 | 110.94 (16) |
| H3A—C3—H3B | 108.1 | N1—C17—C18 | 108.84 (17) |
| O4—C4—O3 | 123.60 (17) | C11—C17—C18 | 112.69 (17) |
| O4—C4—C3 | 122.79 (17) | N1—C17—H17 | 108.1 |
| O3—C4—C3 | 113.59 (16) | C11—C17—H17 | 108.1 |
| C17—N1—H1A | 109.5 | C18—C17—H17 | 108.1 |
| C17—N1—H1B | 109.5 | C17—C18—H18A | 109.5 |
| H1A—N1—H1B | 109.5 | C17—C18—H18B | 109.5 |
| C17—N1—H1C | 109.5 | H18A—C18—H18B | 109.5 |
| H1A—N1—H1C | 109.5 | C17—C18—H18C | 109.5 |
| H1B—N1—H1C | 109.5 | H18A—C18—H18C | 109.5 |
| C16—C11—C12 | 118.73 (18) | H18B—C18—H18C | 109.5 |
| C16—C11—C17 | 119.74 (18) | | |
| O2—C1—C2—O5 | 0.1 (2) | C11—C12—C13—C14 | -0.8 (3) |
| O1—C1—C2—O5 | 179.44 (17) | C12—C13—C14—C15 | 1.5 (3) |
| O2—C1—C2—C3 | 122.75 (18) | C13—C14—C15—C16 | -1.5 (3) |
| O1—C1—C2—C3 | -57.9 (2) | C14—C15—C16—C11 | 0.8 (3) |
| O5—C2—C3—C4 | -57.7 (2) | C12—C11—C16—C15 | -0.2 (3) |
| C1—C2—C3—C4 | 179.19 (15) | C17—C11—C16—C15 | -179.15 (19) |
| C2—C3—C4—O4 | -85.8 (2) | C16—C11—C17—N1 | -116.9 (2) |
| C2—C3—C4—O3 | 92.7 (2) | C12—C11—C17—N1 | 64.2 (2) |
| C16—C11—C12—C13 | 0.2 (3) | C16—C11—C17—C18 | 120.8 (2) |
| C17—C11—C12—C13 | 179.14 (19) | C12—C11—C17—C18 | -58.2 (3) |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| O1—H1...O3 ⁱ | 0.84 | 1.73 | 2.548 (2) | 164 |
| O3—H3...O1 ⁱⁱ | 0.84 | 1.71 | 2.548 (2) | 176 |
| O5—H5...O2 | 0.84 | 2.13 | 2.629 (2) | 118 |
| O5—H5...O4 ⁱⁱⁱ | 0.84 | 2.17 | 2.777 (2) | 129 |

| | | | | |
|---------------------------|------|------|-----------|-----|
| N1—H1A···O1 | 0.91 | 1.96 | 2.865 (2) | 170 |
| N1—H1B···O2 ^{iv} | 0.91 | 1.92 | 2.834 (2) | 178 |
| N1—H1C···O5 ^v | 0.91 | 2.05 | 2.877 (2) | 151 |

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