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# (*R*)-1-Phenylethylammonium 6-amino-5-nitropyrimidine-2,4(1*H*,3*H*)-dionate (*R*)-1-phenylethylamine hemisolvate: hydrogen-bonded sheets of ions with pendent solvent molecules

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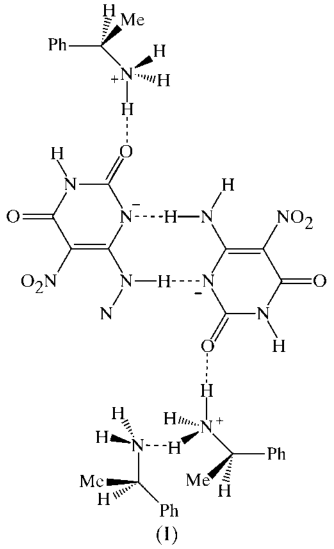
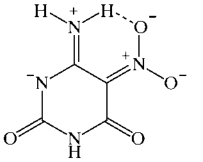
In the title compound, $2C_8H_{12}N^+\cdot 2C_4H_3N_4O_4^-\cdot C_8H_{11}N$, the anions are linked by paired N—H···N hydrogen bonds [H···N = 2.07 and 2.11 Å, N···N = 2.942 (3) and 2.978 (3) Å and N—H···N = 173 and 170°] and by paired N—H···O hydrogen bonds [H···O = 1.98 and 2.05 Å, N···O = 2.855 (3) and 2.917 (3) Å, and N—H···O = 173 and 167°] into chains of rings. These chains are linked into sheets by further N—H···O hydrogen bonds in which all of the donors are provided by the cations [H···O = 1.83–2.17 Å, N···O = 2.747 (3)–2.965 (3) Å and N—H···O = 141–168°]. The neutral amine molecule is pendent from the sheet and is linked to it by a single N—H···N hydrogen bond [H···N = 2.00 Å, N···N = 2.901 (3) Å and N—H···N = 175°].

## Comment

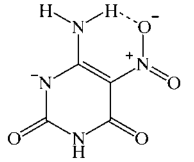
Alkoxy-5-nitrosopyrimidines have proven to be highly activated towards aminolysis of their alkoxy groups, and the aminolysis can be performed at room temperature in a wide variety of solvents, including water (Melguizo *et al.*, 2002). This unusual behaviour has been attributed to the strong electron-withdrawing effect exerted by the 5-nitroso group on pyrimidine atoms C2, C4 and C6. We have therefore sought to establish whether related electron-withdrawing substituents, in particular the nitro group, engender similar activation towards nucleophilic displacement of alkoxy groups by amines. For this purpose, 4-amino-2-methoxy-5-nitropyrimidine-6(1*H*)-one was prepared and treated with a range of primary amines. However, in the case of (*R*)-1-phenylethylamine, the reaction resulted in hydrolysis instead of aminolysis. This can be interpreted as a nucleophilic displacement of the 2-methoxy group by hydroxide, which favourably competed with the aminolysis due to the steric bulk of the amine. A similar example of hydrolysis effectively competing with aminolysis was observed when a 5-nitrosopyrimidine analogue was treated with piperidine (Melguizo *et al.*, 2002).



(I)



(*A*)



(*B*)

The constitution of the title compound, (I), is that of an amine-solvated salt, $2[PhCH(CH_3)NH_3]^+\cdot 2(C_4H_3N_4O_4)^-\cdot PhCH(CH_3)NH_2$, in which all five components of the asymmetric unit lie in general positions. Although the two cations and the single neutral amine component all have an *R* configuration, the substructure generated by the anions alone is very close to being centrosymmetric, although a detailed examination of the hydrogen bonds shows deviations of even this substructure from exact centrosymmetry.

The bond distances in the two independent anions are very similar (Table 1) and both show evidence of considerable electronic polarization. In particular, the C*n*4—N*n*4 ($n$ = 1 or 2) distances are much shorter than those typically found for Ar—$NH_2$ units (mean value = 1.355 Å and lower quartile value = 1.340 Å; Allen *et al.*, 1987), the C*n*5—N*n*5 distances are likewise very much shorter than is normal for Ar—$NO_2$ distances (mean value = 1.468 Å and lower quartile value = 1.460 Å), while the N—O distances are significantly longer than those typically found in nitro groups (mean value = 1.218 Å and upper quartile value = 1.226 Å); in addition, the N*n*5—O*n*51 distances are both longer than the N*n*5—O*n*52 distances. These observations taken together indicate form (*A*) as the dominant contributor to the overall molecular–electronic structure of the anions, with a lesser contribution from form (*B*).

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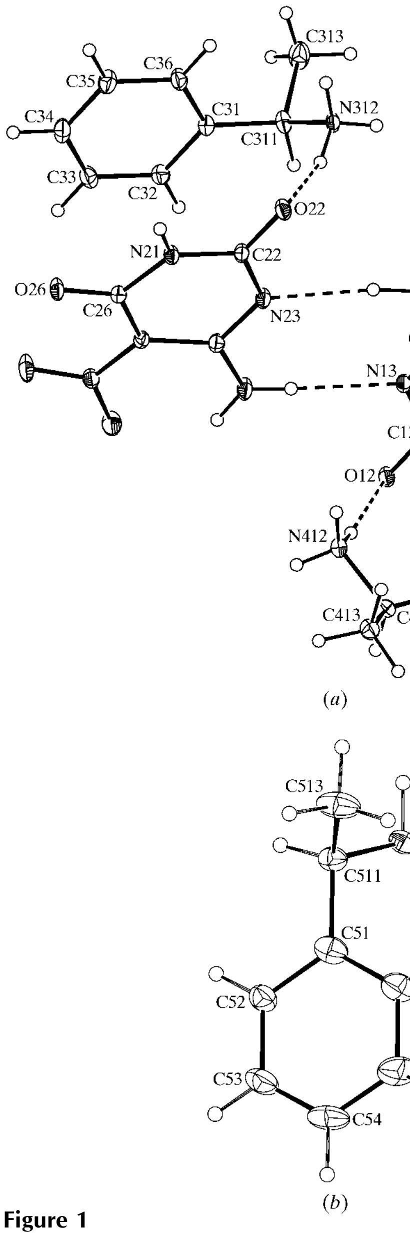
The ionic components form hydrogen-bonded sheets within which the two anions form a one-dimensional substructure in the form of a chain of rings; the chains are linked by the cations, each of which acts a threefold hydrogen-bond donor. However, the neutral amine molecule acts only as a hydrogen-bond acceptor, not as a donor, and it is thus simply pendent from the sheet.

Within the asymmetric unit, atoms N14 and N24 act as hydrogen-bond donors, *via* H14*A* and H24*A*, to N23 and N13, respectively, so generating an $R^2_2(8)$ motif built from paired N—H···N hydrogen bonds (Table 2 and Fig. 1). In addition, atom N11 in the type 1 anion at ($x, y, z$) acts as hydrogen-bond donor to O26 in the type 2 anion at ($1 + x, -1 + y, z$), while N21 in the type 2 anion at ($x, y, z$) acts as donor to O16 in the type 1 anion at ($-1 + x, 1 + y, z$). These two hydrogen bonds thus generate a second $R^2_2(8)$ motif, this time based on paired N—H···O hydrogen bonds, and propagation of these four inter-anion hydrogen bonds generates a $C^2_2(10)C^2_2(10)[R^2_2(8)][R^2_2(8)]$ chain of rings (Bernstein *et al.*, 1995), which runs parallel to the $[1\bar{1}0]$ direction (Fig. 2).



(*a*)

(*b*)

**Figure 1**
The independent components of (I), showing (*a*) the ionic components and (*b*) the neutral amine molecule. Displacement ellipsoids are drawn at the 30% probability level.

The anion chains are linked into sheets by the cations, and two one-dimensional substructures can readily be identified. Ammonium atoms N312 and N412 act as hydrogen-bond donors, *via* H31*B* and H41*B*, to O22 and O12, respectively, within the asymmetric unit. Atom N312 at ($x$, $y$, $z$) acts as donor, *via* H31*A*, to both O26 and O252 at ($1 + x, y, z$) in a planar three-centre N—H···($O_2$) hydrogen bond, which generates a local $R^2_1(6)$ motif, and N412 at ($x$, $y$, $z$) acts as hydrogen-bond donor, *via* H41*A*, to O16 at ($-1 + x$, $y$, $z$). Propagation of these hydrogen bonds then leads to a rather complex molecular ladder running parallel to the [100] direction (Fig. 3). The uprights of this ladder comprise two independent and antiparallel $C^2_2(8)$ chains, with the anion dimers forming the rungs; overall this ladder encloses five different rings, two of $S(6)$ type, an $R^2_2(8)$ ring linking the two independent anions, the $R^2_1(6)$ ring noted above, and a large $R^6_6(24)$ ring between the rungs.

Finally, N312 at ($x$, $y$, $z$) acts as hydrogen-bond donor, *via* H31*C*, to O12 at ($x$, $1 + y$, $z$); propagation of this hydrogen bond, together with the paired N—H···N hydrogen bonds between the anions, generates a $C^3_3(12)[R^2_2(8)]$ chain of rings running parallel to the [010] direction (Fig. 4). The combination of [100], [010] and $[1\bar{1}0]$ chains generates a (001) sheet, but there are no direction-specific interactions between adjacent sheets.

The neutral amine, whose presence may be simply a consequence of filling otherwise void spaces, is linked to the ionic sheets by a single N—H···N hydrogen bond; atom N412 acts as donor, *via* H41*C*, to N512. The hydrogen bonds formed by the two cations are thus different, as N312 acts as donor only to O-atom acceptors (Table 2). Atom N512 does not act

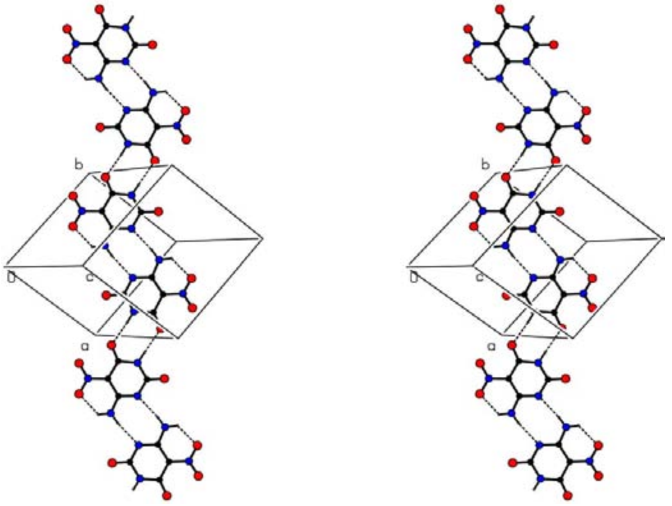


**Figure 2**
Stereoview of part of the crystal structure of (I), showing the formation of a chain of rings along $[1\bar{1}0]$ built from anions only.

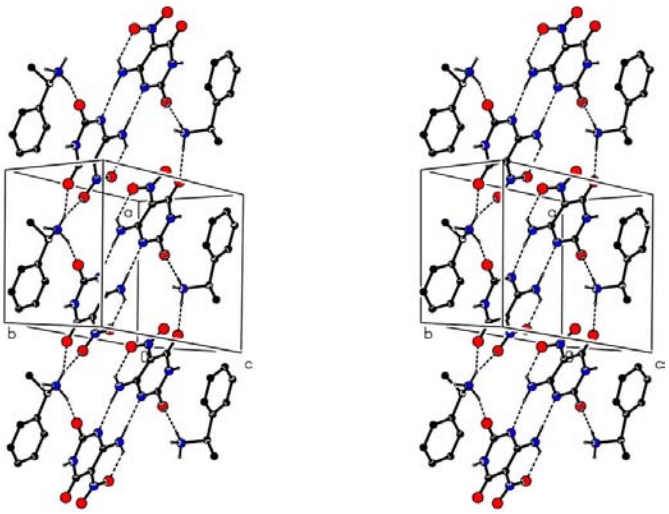


**Figure 3**
Stereoview of part of the crystal structure of (I), showing the formation of a molecular ladder along [100] built from ionic components only. For the sake of clarity, H atoms bonded to C atoms have been omitted.

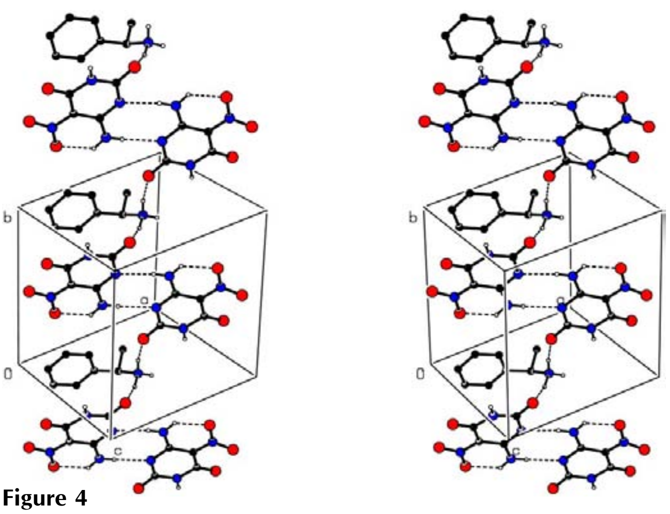


**Figure 4**
Stereoview of part of the crystal structure of (I), showing the formation of a chain along [010]. For the sake of clarity, only the ionic components involved in the chain are shown and H atoms bonded to C atoms have been omitted.

as a donor, either in conventional hard (Desiraju & Steiner, 1999) hydrogen bonds or in N—H$\cdots\pi$(arene) interactions.

## Experimental

4-Amino-2-methoxy-5-nitropyrimidin-6(1*H*)-one was obtained according to the general oxidation procedure described by Taylor & McKillop (1965), consisting of the treatment of a solution of 4-amino-2-methoxy-5-nitrosopyrimidin-6(1*H*)-one in aqueous trifluoroacetic acid with 33% hydrogen peroxide at room temperature. The nitropyrimidine was then treated with a fivefold molar excess of enantiopure (*R*)-1-phenylethylamine in acetonitrile–water (1:1 *v*/*v*), and the resulting mixture was heated until the reactants had completely dissolved. Slow evaporation of the resulting solution yielded crystals of (I) suitable for single-crystal X-ray diffraction.

*Crystal data*

$2C_8H_{12}N^+\cdot 2C_4H_3N_4O_4^-\cdot C_8H_{11}N$
$M_r = 707.76$
Triclinic, $P1$
$a = 8.8183$ (3) Å
$b = 9.6999$ (4) Å
$c = 10.4089$ (5) Å
$\alpha = 86.787$ (2)°
$\beta = 86.377$ (2)°
$\gamma = 78.798$ (3)°
$V = 870.76$ (6) Å$^3$

$Z = 1$
$D_x = 1.350$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3910 reflections
$\theta = 3.0$–27.5°
$\mu = 0.10$ mm$^{-1}$
$T = 120$ (2) K
Prism, colourless
0.40 × 0.30 × 0.18 mm

*Data collection*

Nonius KappaCCD diffractometer
$\varphi$ scans, and $\omega$ scans with $\kappa$ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.958$, $T_{\max} = 0.984$
13 083 measured reflections

3910 independent reflections
3636 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.064$
$\theta_{\max} = 27.5°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.115$
$S = 1.01$
3910 reflections
463 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + 0.1087P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.33$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.31$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| N11—C12 | 1.381 (3) | N21—C22 | 1.379 (3) |
| C12—N13 | 1.333 (3) | C22—N23 | 1.342 (3) |
| N13—C14 | 1.352 (3) | N23—C24 | 1.343 (3) |
| C14—C15 | 1.433 (3) | C24—C25 | 1.441 (3) |
| C15—C16 | 1.441 (3) | C25—C26 | 1.439 (3) |
| C16—N11 | 1.380 (3) | C26—N21 | 1.366 (3) |
| C12—O12 | 1.253 (3) | C22—O22 | 1.245 (3) |
| C14—N14 | 1.326 (3) | C24—N24 | 1.319 (3) |
| C15—N15 | 1.393 (3) | C25—N25 | 1.400 (3) |
| N15—O151 | 1.250 (3) | N25—O251 | 1.258 (3) |
| N15—O152 | 1.237 (3) | N25—O252 | 1.235 (3) |
| C16—O16 | 1.238 (3) | C26—O26 | 1.244 (3) |
| C14—C15—N15—O151 | −12.7 (4) | C24—C25—N25—O251 | 8.0 (4) |
| C14—C15—N15—O152 | 164.3 (2) | C24—C25—N25—O252 | −170.5 (2) |

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

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N14—H14$B\cdots$O151 | 0.88 | 1.97 | 2.604 (3) | 128 |
| N24—H24$B\cdots$O251 | 0.88 | 1.97 | 2.607 (3) | 128 |
| N14—H14$A\cdots$N23 | 0.88 | 2.07 | 2.942 (3) | 173 |
| N24—H24$A\cdots$N13 | 0.88 | 2.11 | 2.978 (3) | 170 |
| N11—H11$\cdots$O26$^{\rm i}$ | 0.88 | 1.98 | 2.855 (3) | 173 |
| N21—H21$\cdots$O16$^{\rm ii}$ | 0.88 | 2.05 | 2.917 (3) | 167 |
| N312—H31$A\cdots$O26$^{\rm iii}$ | 0.85 | 2.04 | 2.747 (3) | 141 |
| N312—H31$A\cdots$O252$^{\rm iii}$ | 0.85 | 2.17 | 2.876 (3) | 141 |
| N312—H31$B\cdots$O22 | 0.97 | 1.83 | 2.763 (3) | 159 |
| N312—H31$C\cdots$O12$^{\rm iv}$ | 0.87 | 1.93 | 2.759 (3) | 158 |
| N412—H41$A\cdots$O16$^{\rm v}$ | 0.86 | 2.06 | 2.906 (3) | 168 |
| N412—H41$B\cdots$O12 | 0.86 | 2.12 | 2.965 (3) | 168 |
| N412—H41$C\cdots$N512 | 0.90 | 2.00 | 2.901 (3) | 175 |

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

The crystals of (I) are triclinic. The space group $P1$ was selected because the chiral amine component was known to be enantiopure. H atoms bonded to C atoms and those bonded to the N atoms in the anions were treated as riding atoms, with N—H distances of 0.88 Å and C—H distances of 0.95 (aromatic), 0.98 ($CH_3$) or 1.00 Å (aliphatic CH). H atoms bonded to N in the amine components were all located from difference maps, and were then allowed to ride on the parent N atoms at the distances deduced from the maps; the resulting distances were in the range 0.85–0.97 Å, with a mean of 0.88 Å, for the cations, and 1.00 and 1.02 Å for the neutral amine molecule. In the absence of any significant anomalous scattering, the Flack (1983) parameter was indeterminate (Flack & Bernardinelli, 2000); hence, the Friedel equivalents were merged before the final refinements and the absolute structure was set by reference to the known $R$ configuration of the amine component.

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 and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1630). Services for accessing these data are described at the back of the journal.

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