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Supramolecular hydrogen-bonded networks in cytosinium succinate and cytosinium 4-nitrobenzoate cytosine monohydrate

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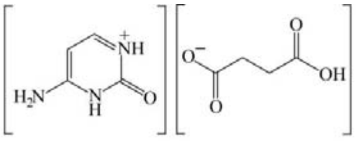
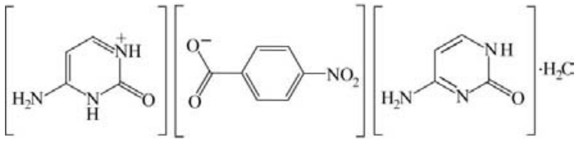
In cytosinium succinate (systematic name: 4-amino-2-oxo-2,3-dihydropyrimidin-1-ium 3-carboxypropanoate), $C_4H_6N_3O^+\cdot C_4H_5O_4^-$, (I), the cytosinium cation forms one-dimensional self-assembling patterns by intermolecular $N-H\cdots O$ hydrogen bonding, while in cytosinium 4-nitrobenzoate cytosine monohydrate [systematic name: 4-amino-2-oxo-2,3-dihydropyrimidin-1-ium 4-nitrobenzoate 4-aminopyrimidin-2(1*H*)-one solvate monohydrate], $C_4H_6N_3O^+\cdot C_7H_4NO_4^-\cdot C_4H_5N_3O\cdot H_2O$, (II), the cytosinium–cytosine base pair, held together by triple hydrogen bonds, leads to one-dimensional polymeric ribbons *via* double $N-H\cdots O$ hydrogen bonds. This study illustrates clearly the different alignment of cytosine molecules in the crystal packing and their ability to form supramolecular hydrogen-bonded networks with the anions.

Comment

The protonated cytosine–cytosine base pair carries important structural implications for biological systems. In particular, this base pair is known to self-assemble in acidic media (Armentano *et al.*, 2004) and is also found in RNA and DNA solutions. Furthermore, X-ray studies have revealed that the cytosine–cytosine base pair contributes to fully intercalated parallel-stranded duplexes of DNA structural motifs in crystals (Kang *et al.*, 1994, 1995). Carboxylic acids belong to an important class of organic molecules and are believed to have existed in the prebiotic earth (Miller & Orgel, 1974; Kvenvolden *et al.*, 1971). Succinic acid may bind to cations in either the monoanionic or the dianionic form, displaying a plethora of interesting structures. Succinic acid, with two carboxyl functions, can exist as a neutral molecule or as single negatively charged or double negatively charged ions (Prasad & Vijayan, 1991). 4-Nitrobenzoic acid can easily lose its acidic H atom and form complexes with other compounds through hydrogen bonding. The present study, reporting the structures of the title compounds, (I) and (II), is a continuation of our ongoing programme on the structure elucidation of nucleobases with carboxylic and aromatic acids



(I)



(II)

In the structures of (I) and (II), the bond lengths and angles (Tables 1 and 3) correspond to those expected for the atom types and the type of hybridization (Allen *et al.*, 1987). The asymmetric unit of (I) contains one cytosinium cation protonated at atom N3 and one succinate anion, with one of the carboxyl groups deprotonated (Fig. 1), while (II) comprises one cytosinium cation (*A*), one cytosine molecule (*B*), one 4-nitrobenzoate anion and one water molecule (Fig. 2). As expected, both the succinate and 4-nitrobenzoate anions of (I) and (II) are planar. In the succinate anion of (I), the two Csp^2-Csp^2 single-bond distances of the carboxylate (C11—C12) and carboxyl (C13—C14) groups are not identical (Table 1). It is of interest to note that the shorter C13—C14 bond links the carboxyl group, while the longer C11—C12 bond links the carboxylate group. The C11—C12—C13—C14 unit is in a *trans* conformation in (I) (Table 1). In the

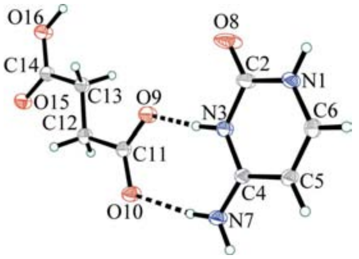


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

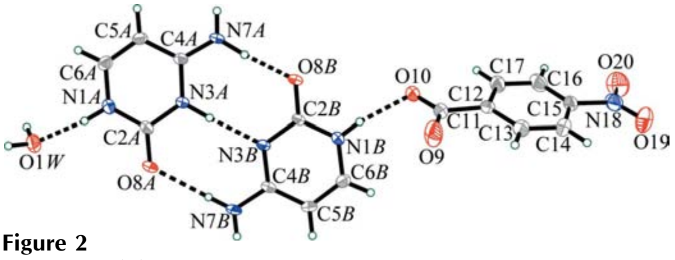


Figure 2
A view of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bond are shown as dashed lines.

4-nitrobenzoate anion of (II), the mean planes of the carboxylate group (C11/O9/O10) and the nitro group (N18/O19/O20) make dihedral angles of 1.9 (3) and 3.8 (2)°, respectively, with the mean plane of the benzene ring (C12–C17). In (I), the O—H bond of the carboxyl group is in a *trans* conformation with respect to the C=O bond, as evidenced from the H16O—O16—C114—O15 torsion angle of 176.9 (6)°.

Cytosine is quite a strong base (pK_{a1} = 1. 6 and pK_{a2} = 12.2; Stecher, 1968) and, in the presence of acids, is readily protonated at the N3 ring position. The molecular geometries of the cytosine and cytosinium cation are in good agreement with those of similar structures (Görbitz & Sagstuen, 2004; Garcia-Teran *et al.*, 2007). The N3 protonation or its absence reflects in the C2—N3—C4 angle. The N3 protonation of the cytosine ring is consistent with the larger C2—N3—C4 angle [124.0 (1)° in (I) and 123.6 (2)° in molecule *A* of (II)], while for unprotonated cytosine the angle is 119.3 (2)°, which agrees well with the reported value of the unprotonated cytosine molecule of 119.4° (McClure & Craven, 1973).

In (I), the cytosinium cation and succinate anion are held together by two N—H···O hydrogen bonds (Table 2), thereby generating an $R_2^2(8)$ motif (Bernstein *et al.*, 1995); this is further interconnected by intermolecular N—H···O and O—H···O interactions involving the cytosinium cations and succinate anions, leading to the formation of a two-dimensional sheet parallel to $(10\overline{1})$ containing $R_4^4(15)$ and $R_4^4(19)$ motifs (Fig. 3). In the case of (II), the cytosinium–cytosine dimers are formed by two N—H···O and one N—H···N hydrogen bonds [$R_4^4(8)$ motif; Table 4], thus resembling a pseudo-Watson–Crick pattern. Furthermore, adjacent cytosinium–cytosine base pairs are interlinked by double N—H···O hydrogen bonds (Table 4), leading to one-dimensional supramolecular polymeric ribbons with alternating neutral and protonated cytosine entities (Fig. 4).

In (II), atom N1 of the cytosinium cation forms an N—H···O hydrogen bond with the water molecule, while the corresponding atom of the cytosine molecule forms an N—H···O hydrogen bond with the 4-nitrobenzoate anion. The water molecule plays a dual role as both donor and acceptor in the hydrogen-bonding interactions (Table 4). It is involved in three hydrogen bonds, acting as donor to two inversion-related 4-nitrobenzoate anions and acceptor to an adjacent cytosinium cation.

In (II), the combination of N—H···O, N—H···N and O—H···O hydrogen bonds involving the cytosinium–cytosine base pairs, the 4-nitrobenzoate anions and the water molecules leads to two-dimensional hydrogen-bonded slots, which extend parallel to the *b* axis. Each slot is arranged like a hexameric hydrogen-bonded network consisting of two sets of parallel cytosinium–cytosine base pairs, which are sandwiched between the two 4-nitrobenzoate anions and two water molecules (Fig. 5). The one-dimensional polymeric ribbon formed by the cytosinium–cytosine base pair interacts with adjacent ribbons through 4-nitrobenzoate anions and water molecules *via* N—H···O and O—H···O hydrogen bonds, thereby generating a two-dimensional supramolecular hydrogen-

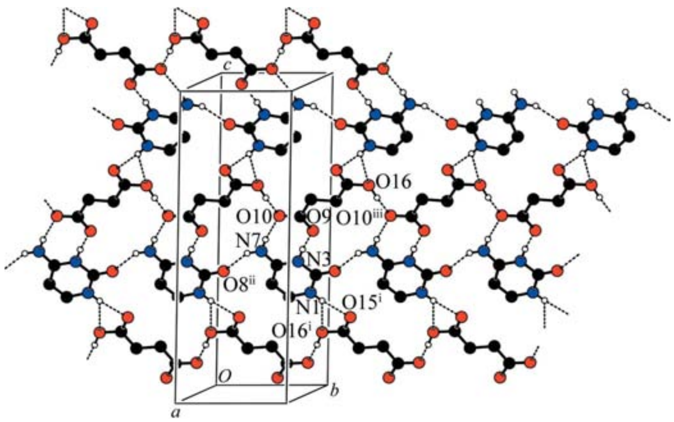


Figure 3
A packing diagram for (I), viewed down the *a* axis. Dashed lines indicate O—H···O and N—H···O hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted for clarity. Only atoms involved in the hydrogen bonds are labelled. [Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{5}{2}, z - \frac{1}{2}$; (ii) $x, y - 1, z$; (iii) $x, y + 1, z$.]

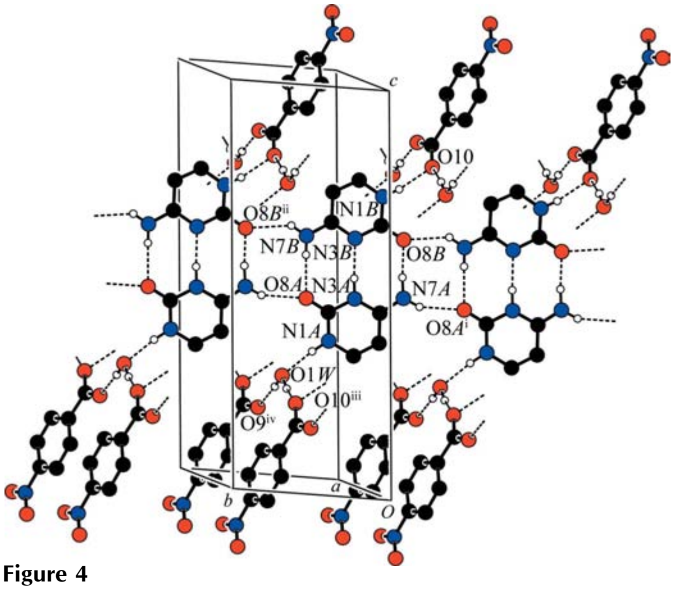


Figure 4
A packing diagram for (II), viewed up the *a* axis. Only atoms involved in the hydrogen bonds are labelled. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $x, y - 1, z$; (ii) $x, y + 1, z$; (iii) $-x + 1, -y, -z + 1$; (iv) $-x + 2, -y, -z + 1$.]

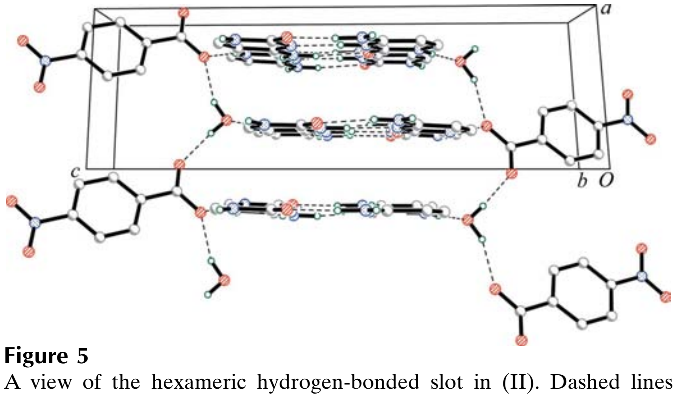


Figure 5
A view of the hexameric hydrogen-bonded slot in (II). Dashed lines indicate O—H···O, N—H···N and N—H···O hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted for clarity.

bonded network parallel to (001). It is very interesting to note that the nitro group of the 4-nitrobenzoate anion does not participate in any conventional hydrogen-bonding interactions. In (II), the water molecule does not have any interaction with the cytosine molecule.

Experimental

To obtain crystals of (I) suitable for X-ray study, cytosine (0.111 g, 1 mmol) and succinic acid (0.118 g, 1 mmol) were dissolved in water (10 ml) and the solution was allowed to evaporate slowly. Crystals of (II) were obtained by slow evaporation of an equimolar solution of cytosine (0.111 g, 2 mmol) and 4-nitrobenzoic acid (0.167 g, 1 mmol) in water (20 ml).

Compound (I)

Crystal data

$C_4H_6N_3O^+\cdot C_4H_5O_4^-$
$M_r = 229.20$
Monoclinic, $C2/c$
$a = 15.666$ (3) Å
$b = 6.6959$ (9) Å
$c = 18.726$ (3) Å
$\beta = 100.480$ (4)°
$V = 1931.5$ (5) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.13$ mm^{-1}
$T = 294$ (2) K
0.23 × 0.17 × 0.13 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
8824 measured reflections
1697 independent reflections
1607 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.108$
$S = 1.10$
1697 reflections
165 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

C11—O9	1.2468 (18)	C11—C12	1.5141 (19)
C11—O10	1.2653 (19)	C13—C14	1.4993 (19)
C11—C12—C13—C14	179.41 (11)		

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O15$^{\rm i}$	0.88 (2)	2.02 (2)	2.9018 (18)	175 (2)
N3—H3N···O9	0.95 (2)	1.65 (2)	2.5916 (15)	172 (2)
N7—H7N···O10	0.91 (2)	2.08 (2)	2.9854 (18)	171.0 (17)
N7—H8N···O8$^{\rm ii}$	0.89 (3)	2.00 (2)	2.8122 (19)	150.5 (19)
O16—H16O···O10$^{\rm iii}$	1.01 (3)	1.51 (3)	2.5250 (16)	176 (2)

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{5}{2}, z - \frac{1}{2}$; (ii) $x, y - 1, z$; (iii) $x, y + 1, z$.

Table 3
Selected bond lengths (Å) for (II).

C11—O9	1.235 (4)	C11—O10	1.248 (3)

Compound (II)

Crystal data

$C_4H_6N_3O^+\cdot C_7H_4NO_4^-\cdot C_4H_5N_3O\cdot H_2O$
$M_r = 407.36$
Triclinic, $P\overline{1}$
$a = 6.7154$ (14) Å
$b = 7.4036$ (16) Å
$c = 19.228$ (4) Å
$\alpha = 85.525$ (4)°
$\beta = 87.576$ (4)°
$\gamma = 67.279$ (3)°
$V = 879.0$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.13$ mm^{-1}
$T = 294$ (2) K
0.19 × 0.16 × 0.08 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
8258 measured reflections
3064 independent reflections
2570 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.209$
$S = 1.10$
3064 reflections
298 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.43$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.45$ e Å^{-3}

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1A···O1W	0.91 (4)	1.80 (4)	2.710 (3)	173 (3)
N3A—H3A···N3B	0.97 (4)	1.88 (4)	2.846 (3)	177 (3)
N7A—H7A···O8$A^{\rm i}$	0.85 (3)	2.11 (3)	2.900 (3)	154 (3)
N7A—H8A···O8B	0.98 (3)	1.76 (3)	2.747 (3)	175 (2)
N1B—H1B···O10	0.85 (4)	1.90 (4)	2.731 (3)	169 (3)
N7B—H7B···O8$B^{\rm ii}$	0.86 (4)	2.18 (4)	2.889 (3)	139 (3)
N7B—H8B···O8A	0.89 (3)	2.06 (3)	2.949 (3)	174 (3)
O1W—H1W···O10$^{\rm iii}$	0.92 (3)	1.97 (3)	2.847 (3)	159 (3)
O1W—H2W···O9$^{\rm iv}$	0.85 (5)	1.87 (5)	2.723 (3)	175 (4)

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

All N- and O-bound H atoms were located in a difference Fourier map and their positions and isotropic displacement parameters were refined. All other H atoms were located in a difference density map but were positioned geometrically and included as riding atoms, with C—H distances in the range 0.93–0.97 Å and with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C).

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL/PC* (Sheldrick, 2008) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3096). Services for accessing these data are described at the back of the journal.

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