organic compounds

Solid-state architecture of saccharin salts of some diamines

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Hydrazinium saccharinate, $N_2H_5^+ \cdot C_7H_4NO_3S^-$, crystallizes in a 1:1 ratio, while ethylenediaminium bis(saccharinate), $C_2H_{10}N_2^{2+} \cdot 2C_7H_4NO_3S^-$, and butane-1,4-diaminium bis(saccharinate), $C_4H_{14}N_2^{2+} \cdot 2C_7H_4NO_3S^-$, form in a 1:2 cation–anion stoichiometry. The structures contain many strong hydrogen bonds of the $N^+-H \cdots N^-$, $N^+-H \cdots O$, $N-H \cdots O$ and $N-H \cdots N$ types, with auxiliary $C-H \cdots O$ interactions.

Comment

Saccharin is a moderately strong acid and its salts have been used as sweeteners for around 125 years (Fahlberg & List, 1887). In recent years, there has been increased interest in the reactivity and structural properties of metal saccharinates because of the potential use of saccharin as an antidote for metal poisoning in the human body (Yilmaz *et al.*, 2004). The corresponding deprotonated saccharinate anion acts as a polyfunctional ligand owing to the presence of imine N, carbonyl O and sulfonyl O atoms. We have recently reported the use of saccharin as a salt former in active pharmaceutical ingredient formulation and development (Banerjee *et al.*, 2005; Bhatt *et al.*, 2005). In this paper, we describe the solid-state architecture of three different amine salts of saccharin, namely hydrazinium saccharinate, (I), ethylenediaminium bis(saccharinate), (II), and butane-1,4-diaminium bis(saccharinate), (III). The amine and saccharin fragments are rich in hydrogen-bond donor and acceptor functionalities. Therefore, it is no surprise that the crystal structures contain many strong hydrogen bonds. Typically, one finds $N^+-H \cdots N^-$, $N^+-H \cdots O$, $N-H \cdots O$ and $N-H \cdots N$ bonds, with auxiliary $C-H \cdots O$ interactions in some cases (Tables 1–3).

Compound (I) crystallizes from methanol in the centrosymmetric space group $P\bar{1}$, with three hydrazinium cations and three saccharinate anions in the asymmetric unit. This structure contains four different types of hydrogen bonds. The molecular geometry and atom numbering of (I) are given in Fig. 1. In this structure, the symmetry-independent hydrazinium cations are connected to one another *via* $N^+-H \cdots N$ hydrogen bonds and form a zigzag array that propagates along the *a* axis. The saccharinate anions are connected with this

zigzag chain *via* various $N^+-H \cdots O$, $N-H \cdots O$, $N-H \cdots N$ and $N^+-H \cdots N$ interactions, giving rise to a complex hydrogen-bonding network (Fig. 2).
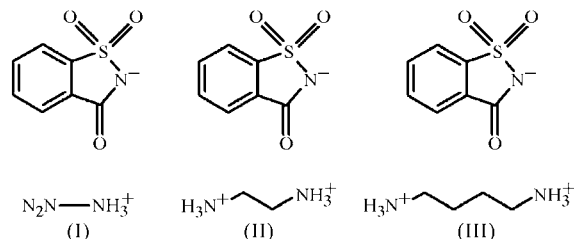
Compound (II) likewise crystallizes in the centrosymmetric space group $P\bar{1}$. However, in this case the asymmetric unit contains one ethylenediaminium cation and two saccharinate anions (Fig. 3). The ethylenediaminium cation adopts the *gauche* conformation, with a dihedral angle between the two
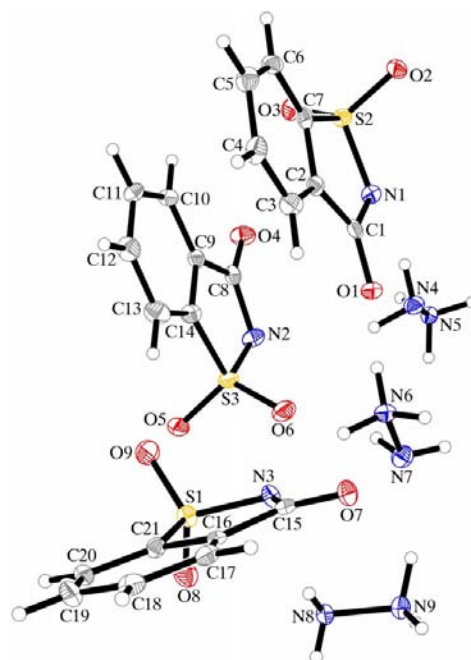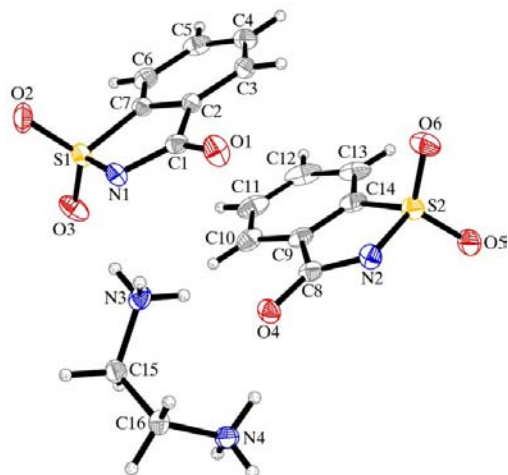

Figure 1
A view of the individual components of (I), showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.
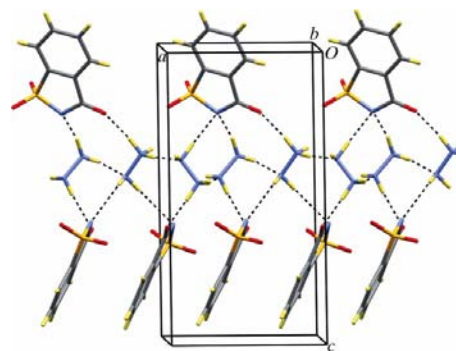
Figure 2
The packing of (I). Note the zigzag chain of hydrazinium cations and the orientations of the saccharinate anions along this helical chain. Hydrogen bonds are shown as dashed lines.
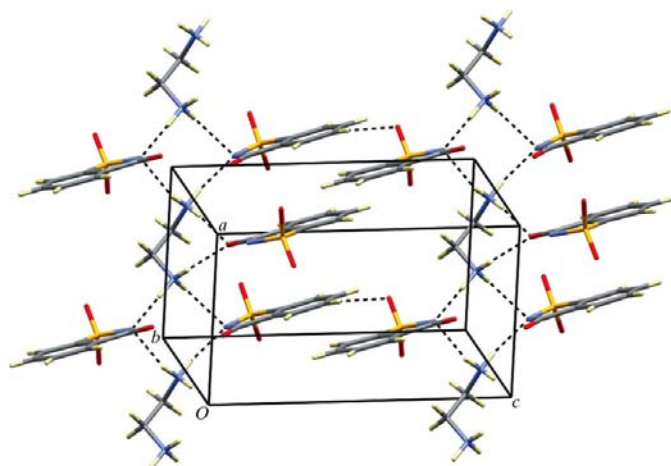
mean planes of 78.3 (3)°. In general, the ethylenediamine molecule adopts the more stable staggered conformation. Among 24 examples in the Cambridge Structural Database (Version 5.27 of November 2005; Allen, 2002), the less stable *gauche* conformation is seen only in seven cases. The crystal structure of the salt is characterized by an eight-membered supramolecular synthon consisting of N^+—$H\cdots N^-$ hydrogen bonds, which propagates along the *a* axis via N^+—$H\cdots O$=C hydrogen bonds (Fig. 4). These hydrogen-bonded layers are connected to one another via C—$H\cdots O$=S hydrogen bonds. Because there are many more hydrogen-bond acceptors than donors in the system, one C=O acceptor of one of the symmetry-independent saccharinate anions remains unsatisfied in terms of hydrogen-bond formation.

Compound (III) crystallizes in the centrosymmetric space group $P2_1/n$. Unlike the ethylenediaminium cation, the butane-1,4-diaminium cation occupies a special position in the unit cell, and the asymmetric unit contains one-half of a butane-1,4-diaminium cation and one saccharinate anion

(Fig. 5). The saccharinate ions form a layered structure, which is characterized by a very stable four-point synthon formed via N^+—$H\cdots O$=S hydrogen bonds. These synthons are connected to one another via another set of N^+—$H\cdots O$=S hydrogen bonds and the pattern propagates along the *ab* plane (Fig. 6). In the crystal structure, the hydrophobic and hydrophilic regions remain separated.

Each of these salts possesses a different crystal packing, although the major intermolecular interactions are similar. The structures described in this paper show that even the smallest structural modification to a molecular component can lead to a completely different crystal structure. A major aim of crystal engineering is to understand the relationship between molecular structure and crystal structure, and to control molecular packing through non-covalent interactions. However, our inability to guide the assembly of many molecules into pre-desired solid-state architectures reflects the delicate nature of the intermolecular interactions that affect molecular assembly. In this sense, prediction of organic crystal structures (Sarma & Desiraju 2002; Dey *et al.*, 2005) remains a major scientific challenge.

Figure 3
A view of the individual compnents of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.
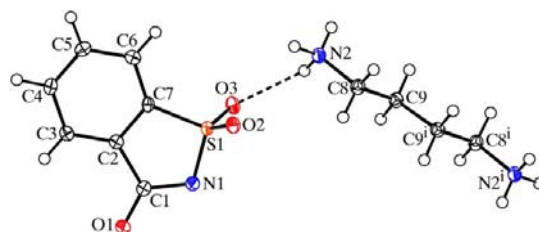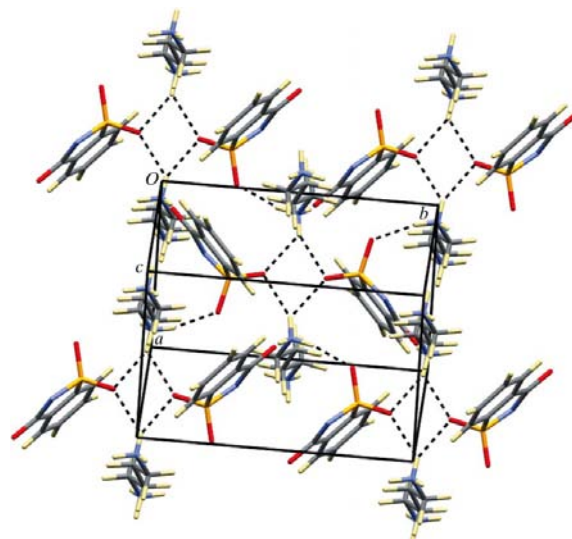

Figure 5
A view of the molecular structure of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $2 - x, 1 - y, -z$.]

Figure 4
The packing of (II); note the N^+—$H\cdots N^-$ tetramer synthon. Hydrogen bonds are shown as dashed lines.

Figure 6
The packing of (III); note the symmetrical N^+—$H\cdots O$=S tetramer synthon. These synthons are connected to each other via another set of N^+—$H\cdots O$=S interactions. Hydrogen bonds are shown as dashed lines.

organic compounds

Experimental

Saccharin (100 mg) was dissolved in ethyl acetate (20 ml) and to this solution were added a few drops of the respective amines until the salt precipitated out. This was filtered off and the residue was dissolved in methanol by warming in a water bath for ten minutes followed by filtration. The filtrate was allowed to cool to room temperature. X-ray quality single crystals were obtained after two days.

Salt (I)

Crystal data

$H_5N_2^+ \cdot C_7H_4NO_3S^-$
$M_r = 215.23$
Triclinic, $P\bar{1}$
$a = 7.8647 (18)$ Å
$b = 11.776 (3)$ Å
$c = 15.904 (4)$ Å
$\alpha = 70.095 (3)°$
$\beta = 87.137 (4)°$
$\gamma = 78.855 (4)°$

$V = 1358.7 (6)$ Å^3
$Z = 6$
$D_x = 1.578$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.34$ mm^{-1}
$T = 100 (2)$ K
Plate, colorless
$0.34 \times 0.29 \times 0.28$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Siemens, 1996)
$T_{min} = 0.888$, $T_{max} = 0.910$

10154 measured reflections
4779 independent reflections
3386 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.118$
$S = 1.00$
4779 reflections
439 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4—H4A⋯O2	0.870 (18)	2.42 (3)	3.097 (4)	135 (3)
N4—H4A⋯N1^i	0.870 (18)	2.40 (3)	3.061 (4)	133 (3)
N4—H4B⋯N2^i	0.88 (4)	2.56 (4)	3.381 (4)	155 (3)
N5—H5A⋯O6^{ii}	0.89 (2)	2.19 (2)	3.008 (4)	154 (3)
N5—H5C⋯O7	0.89 (2)	1.90 (2)	2.789 (4)	172 (3)
N6—H6B⋯O3	0.88 (2)	2.02 (3)	2.787 (4)	145 (4)
N6—H6C⋯O4^{iii}	0.90 (2)	1.84 (2)	2.728 (4)	172 (3)
N7—H7A⋯N3	0.89 (2)	2.43 (2)	3.265 (4)	156 (3)
N7—H7B⋯O4	0.87 (2)	2.12 (3)	2.886 (4)	146 (3)
N8—H8A⋯O1^{iv}	0.89 (2)	1.86 (2)	2.730 (4)	166 (4)
N8—H8C⋯N3	0.90 (2)	2.00 (2)	2.882 (4)	165 (3)
N9—H9A⋯O6^{iv}	0.88 (2)	2.17 (2)	2.975 (4)	152 (3)
N9—H9B⋯O1^i	0.87 (2)	2.10 (2)	2.924 (4)	157 (4)

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

Salt (II)

Crystal data

$C_2H_{10}N_2^{2+} \cdot 2C_7H_4NO_3S^-$
$M_r = 426.46$
Triclinic, $P\bar{1}$
$a = 7.1684 (19)$ Å
$b = 9.964 (3)$ Å
$c = 13.185 (4)$ Å
$\alpha = 84.557 (4)°$
$\beta = 86.387 (4)°$
$\gamma = 76.149 (4)°$

$V = 909.4 (5)$ Å^3
$Z = 2$
$D_x = 1.557$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.34$ mm^{-1}
$T = 100 (2)$ K
Block, colorless
$0.15 \times 0.11 \times 0.06$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Siemens, 1996)
$T_{min} = 0.949$, $T_{max} = 0.979$
10467 measured reflections

3575 independent reflections
2479 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$
$\theta_{max} = 26.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.130$
$S = 0.99$
3575 reflections
277 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.071P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.67$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3A⋯O4	0.87 (3)	1.96 (3)	2.797 (3)	161 (3)
N3—H3B⋯N1	0.91 (3)	2.10 (3)	2.891 (4)	144 (3)
N3—H3B⋯O2^i	0.91 (3)	2.38 (3)	2.981 (4)	123 (2)
N3—H3C⋯N2^{ii}	0.92 (4)	2.19 (4)	3.061 (4)	160 (3)
N4—H4A⋯O4	0.92 (4)	2.02 (4)	2.844 (3)	147 (3)
N4—H4C⋯N1^{iii}	0.90 (4)	2.33 (4)	3.029 (4)	135 (3)
N4—H4B⋯N2^{iv}	0.91 (2)	2.00 (2)	2.899 (4)	169 (3)
N4—H4C⋯O3^v	0.90 (4)	2.30 (4)	2.892 (4)	123 (3)

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

Salt (III)

Crystal data

$C_4H_{14}N_2^{2+} \cdot 2C_7H_4NO_3S^-$
$M_r = 454.52$
Monoclinic, $P2_1/n$
$a = 9.0016 (11)$ Å
$b = 11.2539 (13)$ Å
$c = 10.0269 (12)$ Å
$\beta = 109.196 (1)°$
$V = 959.3 (2)$ Å^3
$Z = 2$

$D_x = 1.574$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.33$ mm^{-1}
$T = 100 (2)$ K
Block, colorless
$0.49 \times 0.37 \times 0.26$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Siemens, 1996)
$T_{min} = 0.857$, $T_{max} = 0.920$
5206 measured reflections

1871 independent reflections
1780 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 26.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.083$
$S = 1.04$
1871 reflections
149 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.7096P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}
Extinction correction: SHELXL97
Extinction coefficient: 0.036 (3)

H atoms on C atoms were refined using a riding model starting from idealized geometries [C—H = 0.93 and 0.99 Å for aromatic and methylene H atoms, respectively, with $U_{iso}(H) = 1.2U_{eq}(C)$]. The

Table 3
Hydrogen-bond geometry (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$B\cdots$O1^i	0.96 (2)	1.91 (2)	2.8173 (17)	158.0 (19)
N2—H2$C\cdots$O2^{ii}	0.89 (2)	1.96 (2)	2.8259 (18)	166.0 (19)
N2—H2$A\cdots$O3^{iii}	0.87 (2)	2.28 (2)	2.9540 (17)	134.9 (18)
N2—H2$A\cdots$O3	0.87 (2)	2.23 (2)	2.9482 (17)	140.3 (17)

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, -y + 1, -z$.

positions of all H atoms on N atoms were taken from a difference Fourier map and refined isotropically.

For all compounds, data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3006). Services for accessing these data are described at the back of the journal.

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