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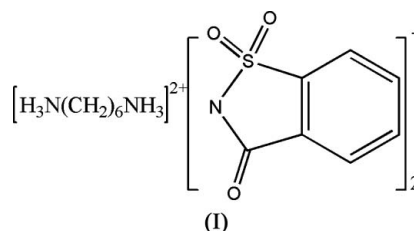
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Key indicators

Single-crystal X-ray study
 $T = 292$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
H-atom completeness 77%
Disorder in main residue
 R factor = 0.052
 wR factor = 0.163
Data-to-parameter ratio = 12.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Hexamethylenediammonium bis(saccharinate):
supramolecular assembly *via* hydrogen bondsThe crystal structure of the title salt, $\text{C}_6\text{H}_{18}\text{N}_2^{2+} \cdot 2\text{C}_7\text{H}_4\text{NO}_3\text{S}^-$, contains two crystallographically independent hexamethylenediammonium dication and two independent saccharinate anions; each of the dication occupies a special position on an inversion centre. The extensive hydrogen-bonding system, involving all six 'active' H atoms, links the anions and cations into an infinite three-dimensional supramolecular assembly.Received 4 January 2006
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Comment

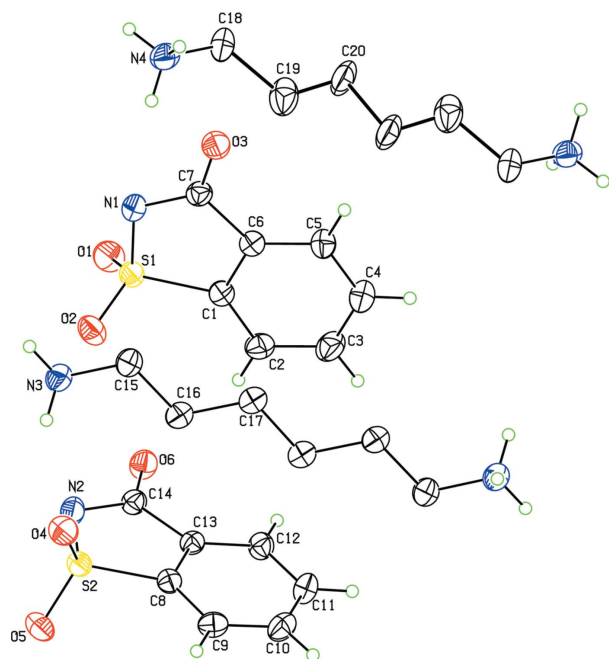
Hydrogen bonding has long been considered to be of importance in biological systems and molecular recognition (Philp & Stoddart, 1996). In recent years, there has been increasing interest in the use of hydrogen bonding for the design and synthesis of supramolecular assemblies and molecular architectures (Prior & Rosseinsky, 2000). However, to the best of our knowledge, no such supramolecular systems have, as yet, been based on the salts of organic bases with the saccharinate anion. Here we describe the structure of hexamethylenediammonium bis(saccharinate), (I), which features a three-dimensional supramolecular hydrogen-bonded assembly.



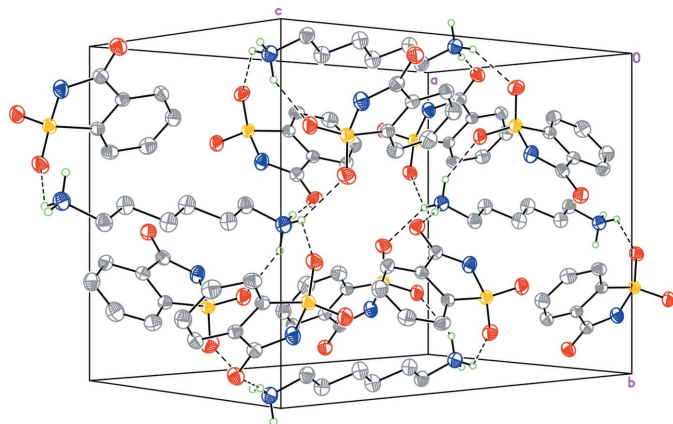
The crystal structure of (I) contains two independent diammonium dication and two saccharinate anions (Fig. 1); each of the dication occupies a special position on an inversion centre. The asymmetric unit of the structure is therefore made up of two half hexamethylenediammonium dication and two saccharinate anions. The cations and anions are held together in the crystal structure through an extensive system of hydrogen bonds (Fig. 2), which involves all six symmetry-independent 'active' H atoms as donors, as well as six O atoms belonging to two saccharinate anions as acceptors (Table 1). These hydrogen bonds link cations and anions into an infinite three-dimensional supramolecular assembly.

Experimental

All reagents were commercially available and of analytical grade. Hexamethylenediamine (1.0 mmol, 0.116 g) was added to an aqueous solution (20 ml) of saccharin (2.0 mmol, 0.376 g). The mixture was stirred for 10 minutes at 353 K. The solution was filtered, and the

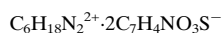
**Figure 1**

The independent ions of (I). Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. H atoms bonded to the C atoms of the hexamethylenediammonium cations as well as the minor occupancy component of the disordered cation have been omitted for clarity. Unlabeled atoms in the N4 cation are related to labeled atoms by $-x, 2 - y, -z$. Unlabeled atoms in the N3 cation are related to labeled atoms by $1 - x, 2 - y, 1 - z$.

**Figure 2**

The crystal packing of (I), viewed down the a axis. Only H atoms bonded to the N atoms are shown. The minor occupancy component of one of the hexamethylenediammonium cations has been omitted.

filtrate was kept at room temperature. After 4 d, colorless crystals of (I) were obtained.

Crystal data
 $M_r = 476.52$

 Monoclinic, $P2_1/c$
 $a = 11.4799$ (10) Å

 $b = 11.5301$ (10) Å

 $c = 16.9116$ (15) Å

 $\beta = 96.499$ (2)°

 $V = 2224.1$ (3) Å³
 $Z = 4$
 $D_x = 1.423$ Mg m⁻³

 Mo $K\alpha$ radiation

Cell parameters from 3509 reflections

 $\theta = 2.4$ – 26.9 °

 $\mu = 0.28$ mm⁻¹
 $T = 292$ (2) K

Irregular fragment, colorless

 $0.20 \times 0.20 \times 0.20$ mm
Data collection

Bruker SMART APEX CCD area-detector diffractometer
 ω scans
 Absorption correction: none
 10895 measured reflections
 3907 independent reflections

3116 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 25.0$ °
 $h = -11 \rightarrow 13$
 $k = -13 \rightarrow 13$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.163$
 $S = 1.08$
 3907 reflections
 310 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0922P)^2 + 0.7478P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.43$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N3-H3A \cdots O2^i$	0.89	2.07	2.872 (3)	149
$N3-H3B \cdots O6^{ii}$	0.89	1.84	2.726 (3)	174
$N3-H3C \cdots O4^i$	0.89	2.45	3.077 (3)	128
$N3-H3C \cdots O1^{iii}$	0.89	2.26	3.041 (3)	147
$N4-H4A \cdots O1^{ii}$	0.89	2.43	3.065 (3)	128
$N4-H4A \cdots O4^i$	0.89	2.25	3.024 (3)	146
$N4-H4B \cdots O3^{iii}$	0.89	1.87	2.757 (3)	178
$N4-H4C \cdots O5^{iv}$	0.89	2.02	2.844 (3)	154

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

All H atoms were placed in calculated positions, with C–H = 0.93 (aromatic) or 0.97 Å (hexane) and N–H = 0.89 Å (amine), and were refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic and hexane H atoms and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$. Initial refinement yielded unusually high displacement parameters for atoms C19 and C20. The difference map revealed peaks of substantial height at possible alternative positions for these two atoms. Introduction of these positions into the refinement produced a significant improvement in the overall precision of the structure. The refinement of the occupancy factors suggested an almost equal contribution of both components of the disorder. In the final refinement, atoms C19 and C20 were included with site-occupancy factors of 0.511(10), while atoms C19' and C20' have site-occupancy factors of 0.489 (10). The two distances C18–C19 and C18–C19' were restrained to be approximately equal; no H atoms were located on any of the disordered atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; 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: *PLATON*.

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