Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

meso-1,2-Diphenylethylenediammonium bis(hydrogen squarate)

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.119
Data-to-parameter ratio = 15.4

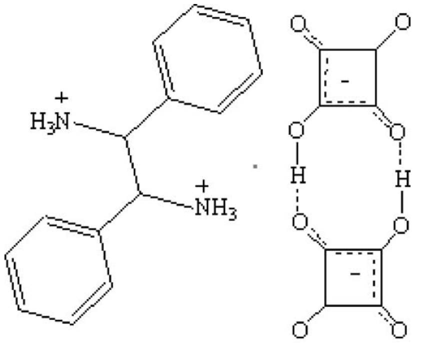
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 29 March 2007
Accepted 11 May 2007

In the title compound, $C_{14}H_{18}N_2^{2+}\cdot 2C_4HO_4^-$, the cation is centrosymmetric. The hydrogen squarate anions form inversion dimers by way of O—H···O links. The cation interacts with the anions by way of N—H···O hydrogen bonds.

Comment

Squaric acid and its salts are useful for the design and synthesis of materials in which the assembly of the structures may be directed mainly by hydrogen bonding, leading to a solid-state array with defined dimensionality. Here, we report the title compound, (I) (Fig. 1), which is a salt of the hydrogen squarate anion with the *meso*-1,2-diphenylethylenediammonium dication, which is comparable with typical metal squarate salts reported previously (Busetti & Lunelli, 1986).



(I)

The asymmetric unit of (I) contains one-half of a centrosymmetric *meso*-1,2-diphenylethylenediammonium cation and one hydrogen squarate (HSQ$^-$) anion. Thus, proton transfer from acid to amine has occurred. The HSQ$^-$ anion has one long C—O bond, two intermediate C—O bonds and one short C—O bond (Table 1). These C—O bond lengths indicate that the degree of delocalization in the HSQ$^-$ ion in (I) is comparable with literature values (Uçar *et al.*, 2004; Bertolasi *et al.*, 2001).

In the crystal structure of (I), pairs of HSQ$^-$ anions form head-to-head inversion dimers *via* O4—H4···O1^{i} [symmetry code: (i) $1 - x$, $1 - y$, $2 - z$] interactions (Table 2), thus forming $R_2^2(10)$ loops (Etter, 1990). The N atom of the cation forms three different N—H···O hydrogen bonds with the O atoms of three symmetrically different HSQ$^-$ species.

Experimental

Squaric acid (0.0285 g) and *meso*-1,2-diphenylethylene diamine (0.0265 g) were dissolved separately in 1:1 aqueous methanol (5 ml)

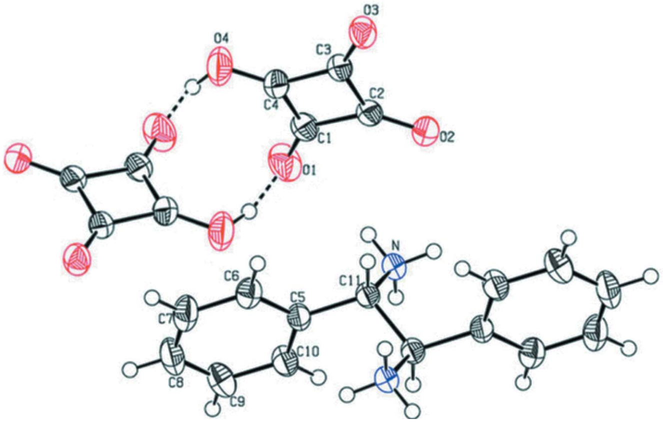


Figure 1
The structure of the constituent ions of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and arbitrary spheres denote H atoms. Dashed lines indicate hydrogen bonds. The unlabelled atoms of the cation are generated by the symmetry operation ($2 - x$, $-y$, $1 - z$) and the unlabelled atoms of the HSQ^- inversion dimer are generated by the symmetry operation ($1 - x$, $1 - y$, $2 - z$).

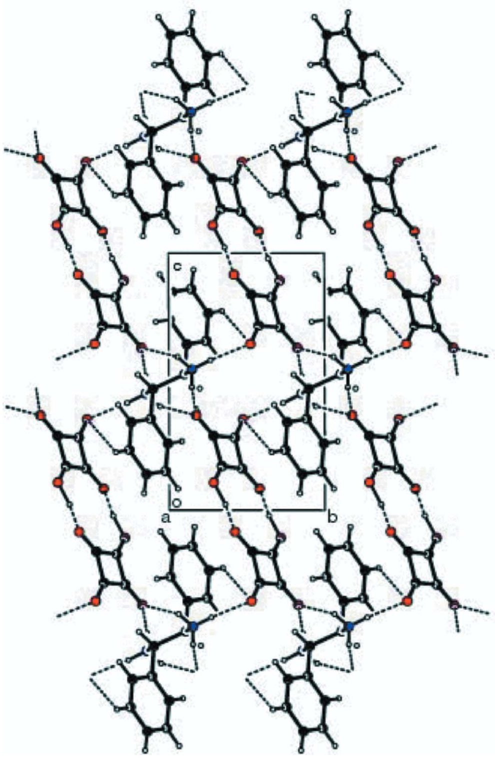


Figure 2
Hydrogen-bonding interactions (dashed lines) in the packing of (I).

and methanol (5 ml), respectively. These solutions were warmed to 333 K and mixed to give a molar ratio of acid-to-amine of 2:1. The resulting mixture was kept at room temperature for slow evaporation of the solvent. Colourless crystals of (I) appeared and these were washed with water and dried *in vacuo*.

Crystal data

$C_{14}H_{18}N_2^{2+}\cdot 2C_4HO_4^-$
$M_r = 440.4$
Triclinic, $P\overline{1}$
$a = 6.3817$ (6) Å
$b = 7.3925$ (7) Å
$c = 11.5034$ (11) Å
$\alpha = 86.765$ (2)°
$\beta = 80.552$ (2)°
$\gamma = 68.420$ (1)°
$V = 497.80$ (8) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 296$ (2) K
$0.35 \times 0.33 \times 0.25$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: none
5658 measured reflections
2276 independent reflections
2144 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.119$
$S = 1.05$
2276 reflections
148 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.28$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

Table 1
Selected bond lengths (Å).

C1—O1	1.2569 (14)	C3—O3	1.2473 (13)
C2—O2	1.2351 (14)	C4—O4	1.2768 (15)

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O1$^{\rm i}$	0.82	1.76	2.5047 (15)	151
N—H1A···O2	0.89	1.94	2.8243 (13)	175
N—H1B···O3$^{\rm ii}$	0.89	2.03	2.8663 (13)	155
N—H1C···O3$^{\rm iii}$	0.89	1.94	2.7780 (13)	156

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

All H atoms were positioned geometrically, with C—H = 0.93–0.98 Å, N—H = 0.89 Å and O—H = 0.82 Å, and refined using a riding model, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(parent).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

RR thanks the Department of Science and Technology, New Delhi, for a Junior Research Fellowship.

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Acta Cryst. (2007). E**63**, o3034–o3035 Ramasubramanian *et al.* • $C_{14}H_{18}N_2^{2+}\cdot 2C_4HO_4^-$ **o3035**