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Picolinamidium squarate and di-*p*-toluidinium squarate dihydrate

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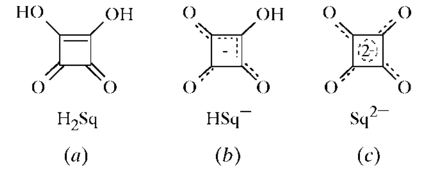
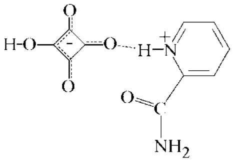
The crystal structure determinations of picolinamidium squarate, $C_6H_7N_2O^+\cdot C_4O_4^-$, (I), and di-*p*-toluidinium squarate dihydrate, $2C_7H_{10}N^+\cdot C_4O_4^{2-}\cdot 2H_2O$, (II), are reported. While salt formation occurs by donation of one H atom from squaric acid to the picolinamide molecule in (I), in compound (II), each squaric acid molecule donates one H atom to the *p*-toluidine N atom of two *trans p*-toluidine molecules. In (I), the pyridine ring is coplanar with the squarate monoanion through imposed crystallographic mirror symmetry; in (II), the dihedral angle between the *p*-toluidine moiety and the squarate dianion is 70.71 (1)°. In (I), a three-dimensional structure is formed *via* van der Waals interactions between parallel planes of molecules, with hydrogen-bond interactions (N—H···O and O—H···O) acting within the planes; hydrogen bonds form a three-dimensional network in (II).

Comment

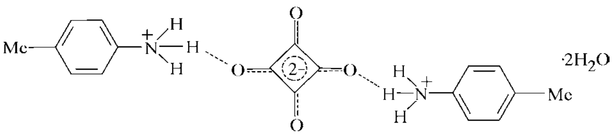
Hydrogen bonding is one of the principal intermolecular interactions that frequently play key roles in molecular recognition and self-assembly (Lehn, 1995; Goswami & Glosh, 1997) as well as in crystal engineering research (Goswami *et al.*, 1998; Desiraju, 2003; Anthony *et al.*, 1998). By choosing appropriate H-atom acceptors and donors, stable intermolecular hydrogen bonds can be formed, thereby providing novel organic systems with unique chemical and physical (optical, magnetic and electronic) properties (Lehn, 1990; Desiraju, 1995; MacDonald & Whitesides, 1994). Hydrogen bonding has been used effectively to predict and design supramolecular assemblies in one, two and three dimensions (Konar *et al.*, 2003; Tao *et al.*, 2003; Felloni *et al.*, 2002). In particular, the combination of different molecules with acid/base properties may make an important contribution to the predictability of the recognition process (Russel *et al.*, 1994; Burchell *et al.*, 2001). Hydrogen-bonded systems generated from organic cations and anions are of special interest because they would be expected to show stronger hydrogen bonds than neutral molecules (Reetz *et al.*, 1994; Bertolasi *et al.*, 2001; Mathew *et al.*, 2002; Bulut *et al.*, 2003). In the present work, we selected the potentially interesting squaric acid and its anions because they are flat and rigid systems.



Squaric acid (H_2Sq) can be found in three forms (see scheme above), *viz*. (*a*) as uncharged H_2Sq, (*b*) as the HSq^- monoanion and (*c*) as Sq^{2-} dianions on deprotonation by amines. These forms have been observed to crystallize with various types of hydrogen bonding, as summarized by Bertolasi *et al.* (2001). In this context, we have synthesized the title compounds, (I) and (II), in which the mono- and dianion forms of squaric acid are observed, and we report the structures of these compounds here. Pyridine-2-carboxamide (picolinamide) and *p*-toluidine, like other organic bases, are protonated in acidic solutions. The bonding of the H atom to the N atoms in (I) and (II) supplies the cationic character.



(I)



(II)

Compound (I) contains one protonated picolinamide cation and one squarate monoanion (HSq^-), with all atoms lying in a crystallographic symmetry-imposed plane (Fig. 1). Each squaric acid molecule donates one H atom to the pyridine N atom of a picolinamide molecule, forming the picolinamidium squarate salt. As seen in Fig. 2, each squarate monoanion links three picolinamide cations in the same plane. In picolinamide

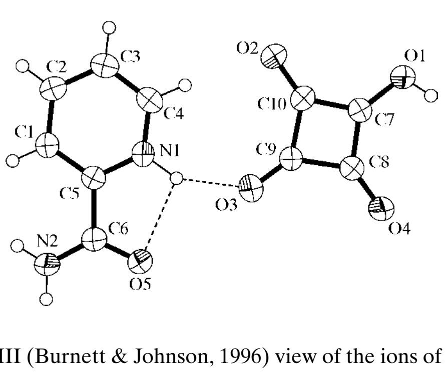


Figure 1
An *ORTEP*III (Burnett & Johnson, 1996) view of the ions of (I), showing the hydrogen bonds, the atom-numbering scheme and 50% probability displacement ellipsoids.

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(Takano *et al.*, 1966), the pyridine ring is almost planar and the angle between the plane of pyridine ring and that of the amine group is about 19°. The difference observed in our study can be attributed to the effect of strong hydrogen bonding. The HSq^- ion has one C—O bond (C7—O1) that is longer than a normal single C—O bond, and two intermediate C—O bonds (C8—O4 and C10—O2), while the C9—O3 bond is typical of a C═O double bond (Table 1). These lengths indicate a degree of delocalization in the HSq^- ion, as has been observed in previous studies (Mathew *et al.*, 2002; Bertolasi *et al.*, 2001).

The crystal packing of (I) is three-dimensional, constructed from van der Vaals interactions between parallel associations of hydrogen-bonded sheets held together by N—H···O and O—H···O interactions (Table 2). O1—H6···O5 and N2—H2*A*···O4 (Table 2) intermolecular hydrogen bonds connect the squarate monoanion to the picolinamide cation, forming a nine-membered ring (Fig. 2). The other O atoms of the HSq^- anion also form hydrogen-bonding interactions with two picolinamide molecules (Fig. 2). The N2···O4 [2.751 (4) Å] distance is shorter than the N1···O3 distance [2.761 (4) Å], in spite of the facts that the formal positive charge resides on the $N1^+H$ group and that positively charged hydrogen bonds are normally stronger (Gilli & Gilli, 2000). A similar situation has been observed in 2-aminopyrimidinium hydrogen squarate (Bertolasi *et al.*, 2001), where such behaviour was attributed to the resonance structure of the HSq^- monoanion (as noted above), with the negative charge not residing on atom O3 but being shared between atoms O2 and O4. In (I), however, there is also a weak intramolecular contact between atoms H5 and O5. The $N2^+$—H2*A*···$O4^{1/2-}$ interaction is the most energetically favoured as a result of the resonance structure of the carboxamide group; the N2—C6 bond length [1.306 (4) Å] is approximately equal to the length of a previously reported C═N double bond (Shanmuga Sundara Raj, Fun, Lu *et al.*, 2000; Shanmuga Sundara Raj, Fun, Zhao *et al.*, 2000). The formal positive charge residing on the $N1^+H$ group does not appear to affect the resonance structure of the pyridine ring. The effect was also observed in the crystal structure of picolinamide (Takano *et al.*, 1966).

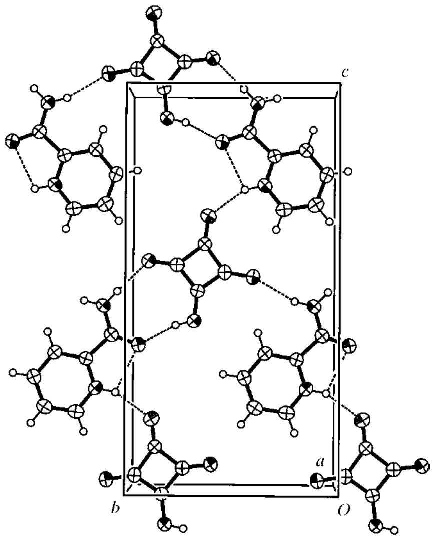

Figure 2
An illustration of the in-plane hydrogen-bonding interactions of (I) in the unit cell. Only one plane is shown for clarity.

In (II), each squaric acid molecule donates one H atom to the *p*-toluidine N atom of two *trans* *p*-toluidine molecules, forming the di-*p*-toluidinium squarate dihydrate salt. The asymmetric unit of (II) contains one protonated *p*-toluidinium cation and one-half of a centrosymmetric squarate dianion, Sq^{2-}, together with an uncoordinated water molecule. A view of (II) and its numbering scheme is shown in Fig. 3. Both the Sq^{2-} ion and the *p*-toluidine moiety are essentially planar, with maximum deviations from these planes being 0.001 (1) Å for atoms C8 and C9, and 0.004 (2) Å for atom C6, while the dihedral angle between the N1/C6/C1/C2 and O1/C8/C9/O2 planes is 70.71 (1)°. The C—O and C—C bond distances in

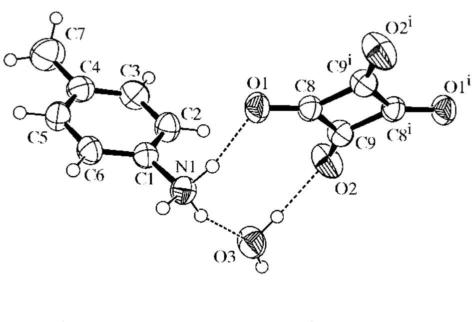

Figure 3
An *ORTEP*III (Burnett & Johnson, 1996) view of the ions of (II), showing the atom-numbering scheme and 50% probability displacement ellipsoids. [Symmetry code: (vi) $-x$, $-y$, $1 - z$.]

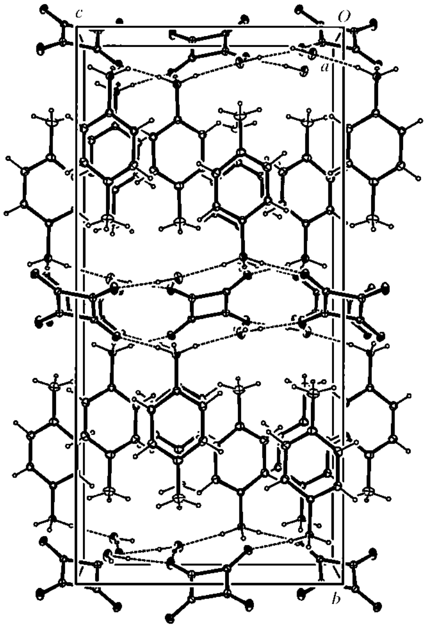

Figure 4
The hydrogen-bonding interactions of (II) in the unit cell; displacement ellipsoids are shown at the 10% probability level.

Sq^{2-} are of equal length (Table 3), indicating aromaticity (Mathew *et al.*, 2002). All the O atoms of the Sq^{2-} ion, the uncoordinated water molecule and the N atom of *p*-toluidine make a contribution to the crystal packing (Table 4). The uncoordinated water molecule links the *p*-toluidine and Sq^{2-} moieties *via* hydrogen-bonding interactions, thus forming an infinite three-dimensional lattice, as shown in Fig. 4.

Experimental

Compound (I) was prepared by mixing squaric acid and picolinamide in a 1:1 molar ratio in a mixed solution of methanol and water (1:1, 50 ml), with stirring at 333 K for 3 h. Crystals of (I) were obtained by slow evaporation of the solvent. The crystals were filtered off, washed with water and methanol, and dried *in vacuo*. Compound (II) was prepared by mixing squaric acid and *p*-toluidine in a 1:2 molar ratio in a mixed solution of methanol and water (1:1, 50 ml), with stirring at 333 K for 3 h. Crystals of (I) were obtained by slow evaporation of the solvent. The crystals were filtered off, washed with water and methanol, and dried *in vacuo*.

Compound (I)

Crystal data

$C_6H_7N_2O^+\cdot C_4HO_4^-$
$M_r = 236.18$
Orthorhombic, *Ima*2
$a = 6.302$ (5) Å
$b = 9.076$ (5) Å
$c = 17.531$ (5) Å
$V = 1002.7$ (10) Å^3
$Z = 4$
$D_x = 1.565$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 5873 reflections
$\theta = 2.3$–28.8°
$\mu = 0.13$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.4 × 0.3 × 0.2 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: by integration (*X-RED*32; Stoe & Cie, 2002)
$T_{min} = 0.965$, $T_{max} = 0.984$
2316 measured reflections

728 independent reflections
589 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 28.8°$
$h = -8 \rightarrow 0$
$k = -12 \rightarrow 12$
$l = -23 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.085$
$S = 1.04$
728 reflections
107 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0611P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.061 (12)

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

C1—C2	1.388 (4)	C7—C8	1.429 (4)
C4—N1	1.324 (4)	C8—O4	1.229 (4)
C5—N1	1.336 (4)	C8—C9	1.498 (4)
C6—N2	1.306 (4)	C9—O3	1.217 (4)
C7—O1	1.312 (4)	C9—C10	1.496 (4)
C7—C10	1.417 (4)	C10—O2	1.243 (3)
N1—C4—C3	120.1 (3)	C7—C10—C9	89.3 (2)
O4—C8—C9	135.0 (3)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$A\cdots$O4^{i}	0.86	1.89	2.751 (4)	179
N2—H2$B\cdots$O2^{ii}	0.86	2.08	2.913 (4)	164
O1—H6$\cdots$O5^{iii}	0.82	1.80	2.602 (3)	165
N1—H5$\cdots$O3	0.88 (3)	1.93 (3)	2.761 (4)	156 (5)
N1—H5$\cdots$O5	0.88 (3)	2.28 (6)	2.633 (4)	104 (4)

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

Compound (II)

Crystal data

$2C_7H_{10}N^+\cdot C_4O_4^{2-}\cdot 2H_2O$
$M_r = 364.40$
Orthorhombic, *Pbca*
$a = 7.761$ (5) Å
$b = 22.288$ (5) Å
$c = 10.684$ (5) Å
$V = 1848.1$ (15) Å^3
$Z = 4$
$D_x = 1.310$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 7934 reflections
$\theta = 1.8$–27.7°
$\mu = 0.10$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.4 × 0.3 × 0.2 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
21 375 measured reflections
2208 independent reflections
1219 reflections with $I > 2\sigma(I)$

$R_{int} = 0.085$
$\theta_{max} = 28.0°$
$h = -10 \rightarrow 9$
$k = -29 \rightarrow 29$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.094$
$S = 0.84$
2208 reflections
140 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.12$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.026 (3)

Table 3
Selected geometric parameters (Å, °) for (II).

C1—N1	1.457 (3)	C8—C9	1.455 (3)
C4—C7	1.513 (4)	C9—O2	1.251 (3)
C8—O1	1.261 (3)		
C3—C4—C7	120.5 (3)	O2—C9—C8	135.4 (2)
C1—C2—C3—C4	−0.2 (4)	O1—C8—C9—O2	0.4 (5)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1	0.97 (3)	1.78 (3)	2.735 (3)	167 (3)
N1—H2$\cdots$O3	0.92 (3)	1.91 (3)	2.788 (3)	159 (3)
N1—H3$\cdots$O1^{i}	0.96 (3)	1.85 (3)	2.806 (3)	174 (2)
O3—H8$\cdots$O2^{ii}	0.98 (4)	1.85 (4)	2.813 (3)	170 (3)
O3—H9$\cdots$O2	0.89 (4)	1.86 (4)	2.751 (3)	173 (3)

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

All H atoms of (I), except atom H5 (on N1), were placed at calculated positions (C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.82 Å) and were allowed to ride on their parent atoms [U_{iso}(H) = 1.2U_{eq}(C) and 1.5U_{eq}(O)]. Atom H5 atom in (I) was located in a difference Fourier map and refined with the N—H distance restrained to 0.87 (3) Å. In (II), the H atoms of the *p*-toluidine moiety (H2/H3/H5/H6 and H7*A*–H7*C*) were located at calculated positions (C—H = 0.93 and 0.96 Å, respectively) and were allowed to ride on their parent atoms [U_{iso}(H) = 1.2U_{eq}(C)]. All other H atoms were refined with isotropic displacement parameters. The H atoms on atom N1 were positioned from a difference map and refined with the N—H distance restrained to 0.87 (3) Å.

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997) for (I) and *SIR*97 (Altomare *et al.*, 1999) for (II); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1062). Services for accessing these data are described at the back of the journal.

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