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Dinicotinamidium squarate

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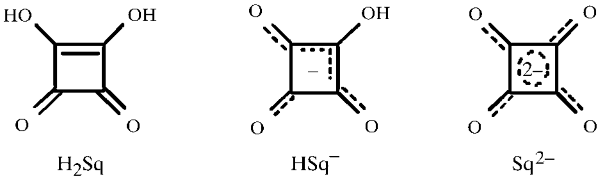
The crystal structure determination of the dinicotinamidium squarate salt, $2C_6H_7N_2O^+\cdot C_4O_4^{2-}$, is reported, with the squarate dianion residing on an inversion centre and the unique cation in a general position. Salt formation occurs by donation of two H atoms from squaric acid to the nicotinamide base. The crystal packing is derived from three types of hydrogen bonding. The primary hydrogen bond involves a squarate anion O atom and an H atom of the protonated pyridine group of the nicotinamide, with an N$\cdots$O distance of 2.5760 (13) Å. The second hydrogen bond involves a second anion O atom and an amide H atom, with an N$\cdots$O distance of 2.8374 (14) Å. Thirdly, an intermolecular interaction between two coplanar nicotinamide moieties occurs between an amide O atom and a symmetry-related amide H atom, with an N1$\cdots$O3 distance of 2.8911 (15) Å. These hydrogen bonds are also responsible for the planarity of the nicotinamide moiety in the salt.

Comment

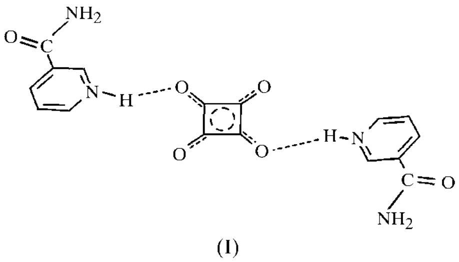
It is known that hydrogen bonding is the most probable means of generating a supramolecular organic system (Lehn, 1995; Desiraju, 1989). These systems have been shown to have unique chemical and physical properties (Desiraju, 1995; MacDonald & Whitesides, 1994). Hydrogen bonding also plays a crucial role in molecular recognition (Goswami & Ghosh, 1997) and crystal-engineering research (Goswami *et al.*, 1998). In particular, the combination of different molecules with acid/base properties might make an important contribution to the predictability of the recognition process (Russell *et al.*, 1994; Burchell *et al.*, 2001). The design of highly specific solid-state structures formed by hydrogen bonding finds significant application in organic chemistry, such as in the development of new optical, magnetic and electronic systems (Lehn, 1990). In this context, squaric acid and its anions are of potential interest because they are flat and rigid systems.

Squaric acid can crystallize in three forms, as shown in Scheme 1. It can crystallize as uncharged H_2SQ, or also as HSQ^- or SQ^{2-} anions on deprotonation by amines. These three forms of squaric acid have been observed to crystallize by various types of hydrogen bonding, which are summarized in the work of Bertolasi (Bertolasi *et al.*, 2001). Squaric acid donates one or two H atoms (although this is not common) to planar aromatic bases, forming so-called low-barrier hydrogen bonds (LBHBs; Cassidy *et al.*, 1999) or positive/negative charge-assisted hydrogen bonds [(+/−)-CAHB; Gilli *et al.*, 1996]. The present study reports an example of this type of hydrogen bonding, in which squaric acid donates two H atoms to a planar nicotinamide base, forming the title dinicotinamidium squarate salt, (I).



Scheme 1

The asymmetric unit of (I) contains one protonated nicotinamide cation and half of a centrosymmetric squarate anion (SQ^{2-}). A view of the hydrogen-bonded structure of (I) and its numbering scheme are shown in Fig. 1. Both the squarate and the nicotinamide moieties are planar and the dihedral angle between these planes is 87.54 (6)°. In (I), it is observed that the squarate anion is surrounded by four nicotinamide cations. This is formed such that each squaric acid molecule gives two H atoms to the pyridine N atom of two *trans* nicotinamide moieties lying parallel to each other, since nicotinamide, like other organic bases, is protonated in acidic solution.



(I)

Each O atom of the SQ^{2-} anion makes a contribution to the crystal packing (Fig. 2). The hydrogen bond between squarate atom O2 [and O2^i; symmetry code: (i) $1-x, 2-y, 1-z$] and the protonated pyridine part of the nicotinamide is quite strong [N2—H2$\cdots$O2 = 2.5760 (13) Å] and potentially belongs to the class of N2$^+$—H$\cdots$O low-barrier hydrogen bonds (Cassidy *et al.*, 1999). This strong hydrogen bond connects two planar *trans* nicotinamidium moieties in parallel planes and is also the reason for the longer N2—H2 distance of 1.08 (2) Å. Atom O1 of the SQ^{2-} anion interacts with atom H1*B* of the amide part of the nicotinamide [N1—H1*B*$\cdots$O1 = 2.8374 (14) Å]. There is also an intermolecular hydrogen bond that links the nicotinamide dimers [N1—H1*A*$\cdots$O3 =

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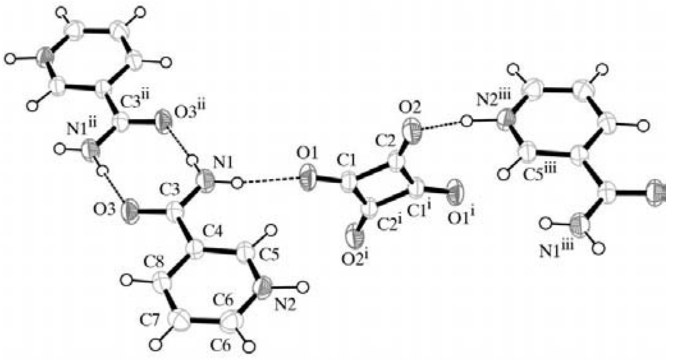

Figure 1
A view of the ionic moieties of (I), illustrating the atom-numbering scheme and the hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The hydrogen bonds are indicated by dashed lines [symmetry codes: (i) $-x$, y, $\frac{1}{2}-z$; (ii) $2-x$, $1-y$, $1-z$; (iii) $1-x$, $2-y$, $1-z$].

2.8911 (15) Å] and forms an eight-membered ring in the structure of (I). This hydrogen bond keeps the two nicotinamide moieties in the same plane.

The C3—C4 bond [1.4959 (17) Å] links the pyridine and amide moieties, and it is similar to that found in a gas-phase electron-diffraction study of nicotinamide [1.498 (8) Å; Takeshima *et al.*, 2003]. A comparison of equivalent bond distances involving the pyridine ring atoms of (I) with the values found in the above-cited gas-phase study shows that the positive charge is localized on the pyridine N atom and does not have much effect on the resonance structure of the pyridine. The skeletal structure of nicotinamide is non-planar, with a C5—C4—C3—N1 torsion angle of 34° in the gas phase and 23° in a neutron diffraction study (Miwa *et al.*, 1999). However, this angle is 0.59 (19)° in the present study, indicating that the nicotinamide moiety in the title salt is almost planar, and this can be attributed to the effect of hydrogen bonding. The nicotinamide C=O bond length in the present salt is 0.017 Å longer than that in the gas phase, while the amide C—N bond length in the solid state is 0.021 Å shorter than that in the gas phase. These changes are close to the values observed for benzamide (Takeuchi *et al.*, 1999) and they are ascribed to the effects of hydrogen bonding on the crystal structure.

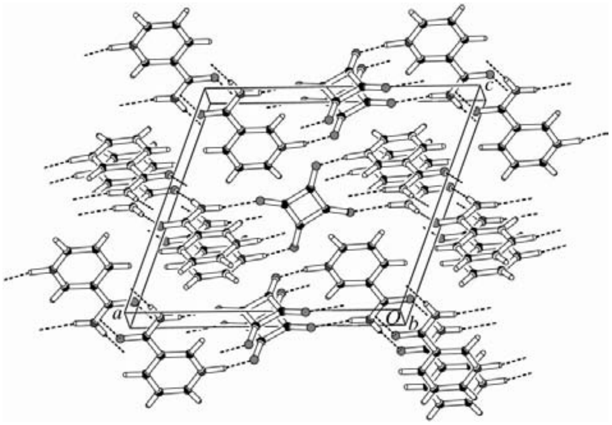

Figure 2
The three-dimensional structure of (I), linked by hydrogen bonds.

Experimental

Compound (I) was prepared by mixing nicotinamide and squaric acid in a 1:1 molar ratio in a mixed solution of methanol and water (1:1, 100 ml) with stirring at 333 K for 12 h. Crystals of (I) were obtained by slow evaporation of the solvent. The crystals were filtered off, washed in water and methanol, and dried *in vacuo*.

Crystal data

$2C_6H_7N_2O^+\cdot C_4O_4^{2-}$
$M_r = 358.32$
Monoclinic, $P2_1/c$
$a = 13.2377$ (15) Å
$b = 5.3623$ (4) Å
$c = 11.5142$ (16) Å
$\beta = 109.822$ (10)°
$V = 768.90$ (15) Å^3
$Z = 2$
$D_x = 1.548$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6059 reflections
$\theta = 0.0$–29.5°
$\mu = 0.12$ mm^{-1}
$T = 293$ (2) K
Plate, yellow
0.48 × 0.31 × 0.08 mm

Data collection

Stoe IPDS-2 diffractometer
Rotation scans
Absorption correction: by integration (*X-RED*32; Stoe & Cie, 2002)
$T_{\min} = 0.938$, $T_{\max} = 0.985$
2140 measured reflections
2140 independent reflections
1497 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 29.5$°
$h = -18 \rightarrow 17$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.109$
$S = 0.90$
2140 reflections
146 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0779P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—O1	1.2422 (14)	C3—C4	1.4959 (17)
C2—O2	1.2571 (16)	C5—N2	1.3361 (16)
C3—O3	1.2367 (13)	C6—N2	1.3337 (17)
C3—N1	1.3272 (16)		
O1—C1—C2	134.20 (12)	O3—C3—C4	118.72 (11)
O2—C2—C1	132.83 (12)	N1—C3—C4	118.65 (10)
O3—C3—N1	122.62 (12)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O2^{i}	1.08 (2)	1.51 (2)	2.5760 (13)	169 (2)
N1—H1*A*···O3^{ii}	0.920 (19)	1.974 (19)	2.8911 (15)	175.3 (16)
N1—H1*B*···O1	0.882 (16)	1.961 (17)	2.8374 (14)	171.8 (15)

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

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All H atoms were found in a difference map and their parameters were refined freely. C—H bond distances were in the range 0.971 (14)–1.015 (16) Å, with $U_{\rm iso}$(H) values in the range 0.036 (4)–0.057 (5) Å^2. The N1—H1*B* and N1—H1*A* bond distances were 0.880 (18) and 0.921 (17) Å, respectively, with $U_{\rm iso}$(H) values of 0.045 (4) and 0.057 (5) Å^2, respectively. The deviation of the N2—H2 bond distance [1.08 (2) Å, with $U_{\rm iso}$(H) = 0.079 (6) Å^2] from a normal value was attributed to the strong N2···O2 hydrogen bond [2.5760 (13) Å].

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); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *PLATON* (Spek, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1196). Services for accessing these data are described at the back of the journal.

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