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General rules for the packing of hydrogen-bonded crystals as derived from the analysis of squaric acid anions: aminoaromatic nitrogen base co-crystals

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Preparation and single-crystal X-ray structure determination of three co-crystals of hydrogen squarate, HSQ^-, with 2-aminopyrimidine, 3-aminopyridine and 4-aminopyridine, and one of squarate, SQ^{2-}, with 8-aminoquinoline are reported. Their crystal packings are analyzed and discussed in terms of the intermolecular O—H···O, N—H···O/N and C—H···O hydrogen bonds formed. Although the fine details of the supramolecular architecture are barely rationalizable, the comparative analysis of the data makes it possible to suggest some simple rules that may be of general application for the packing of hydrogen-bonded crystals, *i.e.* **Rule 1**: 'All hydrogen-bond acceptors available in a molecule will be engaged in hydrogen bonding as far as there are available donors'; **Rule 2**: 'The hydrogen-bond acceptors will be saturated in order of decreasing strength of the hydrogen bonds formed'.

1. Introduction

The most recent attempts at the crystal engineering of molecular crystals (Desiraju, 1989) is largely based on the arrangements of building blocks (tectons; Simars *et al.*, 1991) consisting of molecules or ions which present complementary molecular interactions (supramolecular synthons; Desiraju, 1995). In order to produce stable co-crystals it is therefore indispensable to have a detailed knowledge of the forces that may determine the structural motifs of the crystalline materials. Hydrogen bonds, in view of their energy and directionality, are among the most important forces utilized by the molecules to interact (Etter, 1990; Bertolasi *et al.*, 1995; Jeffrey, 1997) and the formation of co-crystals is often directed by heteromolecular hydrogen bonds which turn out to be stronger than the homomolecular ones (Desiraju & Sharma, 1995). In particular, the mixing of couples of molecules with acid/base properties may make a crucial improvement in the predictability of the recognition processes owing to the dominating contribution of charge-assisted hydrogen bonds (Russell *et al.*, 1994; Aakeröy *et al.*, 1996; Burchell *et al.*, 2001).

Squaric acid, H_2SQ, is a molecule frequently used to build up co-crystals with organic bases to give specific two- or three-dimensional aggregates (Reetz *et al.*, 1994; Karle *et al.*, 1996; Angelova *et al.*, 1996; Bouma *et al.*, 1999; McLean, Wheatley, Ferguson & Glidewell, 1999; McLean, Wheatley, Ferguson, Glidewell & Lough, 1999). Being a strong diprotic acid (pK_1 = 1.2–1.7; pK_2 = 3.2–3.5; Ireland & Walton, 1967; MacDonald, 1968) it can crystallize as H_2SQ (Semmingsen *et al.*, 1977; Gilli & Bertolasi, 1990) as well as HSQ^- or SQ^{2-} anions, the last

Table 1
Experimental details.

	(1)	(2)	(3)	(4)
Crystal data				
Chemical formula	$C_4H_6N_3{\cdot}C_4HO_4$	$C_5H_7N_2{\cdot}C_4HO_4$	$C_5H_7N_2{\cdot}C_4HO_4$	$C_9H_9N_2{\cdot}1/2(C_4O_4)$
Chemical formula weight	209.17	208.18	208.17	201.2
Cell setting, space group	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/c$	Triclinic, $P\overline{1}$
a, b, c (Å)	8.279 (1), 10.184 (1), 5.353 (2)	3.812 (1), 11.012 (2), 21.942 (5)	10.283 (3), 7.068 (1), 12.642 (2)	7.209 (1), 7.861 (1), 8.443 (1)
α, β, γ (°)	99.72 (2), 104.05 (2), 87.73 (1)	100.78 (2), 91.66 (2), 88.26 (2)	90, 97.95 (2), 90	108.07 (1), 91.62 (1), 89.83 (1)
V (Å^3)	431.5 (2)	904.1 (4)	910.0 (3)	454.7 (1)
Z	2	4	4	2
D_x (Mg m^{-3})	1.610	1.529	1.519	1.470
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	25	25	25	25
θ range (°)	8–14	8–13	9–13	7–13
μ (mm^{-1})	0.132	0.123	0.122	0.104
Temperature (K)	296 (2)	296 (2)	296 (2)	296 (2)
Crystal form, colour	Plate, colourless	Prism, pale yellow	Irregular, colourless	Irregular, brown
Crystal size (mm)	0.52 × 0.36 × 0.10	0.52 × 0.30 × 0.14	0.60 × 0.36 × 0.28	0.50 × 0.40 × 0.38
Data collection				
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans
No. of measured, independent and observed parameters	2769, 2078, 1596	4454, 3913, 2471	2995, 2647, 2216	2828, 2628, 2310
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.013	0.022	0.030	0.010
$\theta_{\rm max}$ (°)	28.00	27.00	30	29.97
Range of h, k, l	$0 \rightarrow h \rightarrow 10$ $-13 \rightarrow k \rightarrow 13$ $-7 \rightarrow l \rightarrow 6$	$0 \rightarrow h \rightarrow 4$ $-13 \rightarrow k \rightarrow 14$ $-28 \rightarrow l \rightarrow 27$	$0 \rightarrow h \rightarrow 14$ $0 \rightarrow k \rightarrow 9$ $-17 \rightarrow l \rightarrow 17$	$0 \rightarrow h \rightarrow 10$ $-10 \rightarrow k \rightarrow 11$ $-11 \rightarrow l \rightarrow 11$
No. and frequency of standard reflections	3 every 120 min	3 every 120 min	3 every 120 min	3 every 120 min
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0498, 0.1496, 1.016	0.064, 0.2029, 1.056	0.0379, 0.1186, 1.072	0.043, 0.1295, 1.056
No. of reflections and parameters used in refinement	2078, 164	3913, 336	2647, 169	2628, 172
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1114P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1236P)^2 + 0.1121P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0708P)^2 + 0.1027P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0847P)^2 + 0.0419P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$	0.003	0.018	0.006	0.012
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (e Å^{-3})	0.341, −0.33	0.347, −0.388	0.367, −0.175	0.269, −0.271
Extinction method	None	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)	None
Extinction coefficient	–	0.011 (4)	0.036 (5)	–

Computer programs used: *CAD*-4 (Enraf–Nonius, 1984), *MolEN* (Fair, 1990), *SIR*92 (Altomare *et al.*, 1994), *SHELXL*97 (Sheldrick, 1997).

two being particularly suited to interact with molecules rich in hydrogen-bond donors such as the aminoaromatic bases presently investigated, which can be hydrogen-bond donors both by the aminic group and the aromatic $\equiv N^+H$ function obtained by proton transfer from the squaric acid itself. In general, squaric acid and its anions are of potential interest in crystal engineering because of their nature of small, flat and rigid molecules which can self-assemble by strong $\cdots O{=}C{-}C{=}C{-}OH\cdots$ resonance-assisted hydrogen bonds (RAHBs; Gilli *et al.*, 1989; Gilli *et al.*, 1993; Bertolasi *et al.*, 1996) in H_2SQ and HSQ^-, or even stronger $-O{-}H\cdots O^-$ [negative charge-assisted hydrogen bonds (−)CAHB] (Gilli *et al.*, 1994, 1996) in HSQ^- and, moreover, may be acceptors of further hydrogen bonds donated by aminic, iminic and hydroxilic functions. Finally, squaric acid may donate one or two protons to planar aromatic nitrogen bases forming $\equiv N^+H\cdots O^-$ bonds which potentially belong to the class of $\equiv N^+H\cdots O^- \leftrightarrow \equiv N\cdots HO$ bonds which are often called LBHBs (low-barrier hydrogen bonds; Cleland & Kreevoy, 1994; Cassidy *et al.*, 1999) or (+/−)CAHB (positive/negative charge-assisted hydrogen bonds; Gilli *et al.*, 1994, 1996), and whose strength is determined by the matching of the pK_a values of the squaric acid and of the base involved.

The present paper reports the crystal structures of four adducts between squaric acid and aminoaromatic bases, *i.e.* 2-amino-1,3-pyrimidine, 3-amino- and 4-aminopyridine and 8-aminoquinoline, which are found to form either $(HSQ^-)_2$ dimers or SQ^{2-} isolated anions. It is shown that the crystal packing analysis of these co-crystals seems able to suggest some rules of general validity for all crystals whose supramolecular architecture is dominated by hydrogen-bond formation.

2. Experimental

Squaric acid and aminoaromatic nitrogen bases were dissolved in water/ethanol mixture in the molar ratio 1:1 for (1)–(3) and 1:2 for (4), and allowed to crystallize slowly at room temperature. Crystal data, data collection and refinement details are given in Table 1.[1] X-ray diffraction data were collected at room temperature on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å) with $\omega/2\theta$ scans. Lattice constants were determined by least-squares fitting of the setting angles of 25 reflections in the range $9 \leq \theta \leq 14°$. The intensities of three

Table 2
Selected bond distances (Å).

(1)			
O1—C1	1.304 (2)	N1—C5	1.351 (2)
O2—C2	1.259 (2)	N1—C6	1.346 (2)
O2—C3	1.223 (2)	N2—C5	1.347 (2)
O4—C4	1.220 (2)	N2—C8	1.316 (2)
C1—C2	1.405 (2)	N3—C5	1.312 (2)
C1—C4	1.445 (2)	C6—C7	1.351 (3)
C2—C3	1.470 (2)	C7—C8	1.392 (2)
C3—C4	1.516 (2)		
(2)			
O11—C11	1.307 (3)	O12—C12	1.307 (4)
O21—C21	1.240 (3)	O22—C22	1.239 (3)
O31—C31	1.215 (3)	O32—C32	1.198 (4)
O41—C41	1.242 (3)	O42—C42	1.239 (3)
C11—C21	1.434 (3)	C12—C22	1.431 (4)
C11—C41	1.412 (4)	C12—C42	1.425 (4)
C21—C31	1.480 (4)	C22—C32	1.496 (4)
C31—C41	1.485 (3)	C32—C42	1.490 (4)
N11—C81	1.329 (4)	N12—C82	1.307 (4)
N11—C91	1.322 (4)	N11—C92	1.353 (4)
N21—C51	1.344 (4)	N22—C52	1.348 (4)
C51—C61	1.404 (4)	C52—C62	1.392 (4)
C51—C91	1.398 (3)	C52—C92	1.400 (4)
C61—C71	1.346 (4)	C62—C72	1.378 (4)
C71—C81	1.386 (4)	C72—C82	1.379 (4)
(3)			
O1—C1	1.309 (1)	N1—C7	1.338 (2)
O2—C2	1.249 (1)	N1—C8	1.343 (2)
O3—C3	1.225 (1)	N2—C5	1.336 (1)
O4—C4	1.232 (1)	C5—C6	1.411 (2)
C1—C2	1.423 (1)	C5—C9	1.410 (1)
C1—C4	1.441 (1)	C6—C7	1.363 (2)
C2—C3	1.482 (1)	C8—C9	1.360 (2)
C3—C4	1.503 (1)		
(4)			
O1—C1	1.256 (1)	C4—C5	1.358 (2)
O2—C2	1.243 (1)	C5—C6	1.417 (2)
C1—C2	1.465 (2)	C6—C7	1.420 (1)
C1—C2′	1.459 (2)	C6—C8	1.407 (2)
N1—C3	1.328 (2)	C7—C11	1.429 (2)
N1—C7	1.369 (1)	C8—C9	1.364 (2)
N2—C11	1.367 (1)	C9—C10	1.402 (2)
C3—C4	1.392 (2)	C10—C11	1.387 (1)

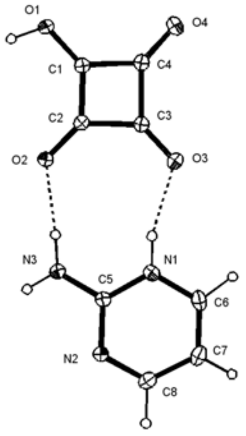


Figure 1
The molecular components of (1), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

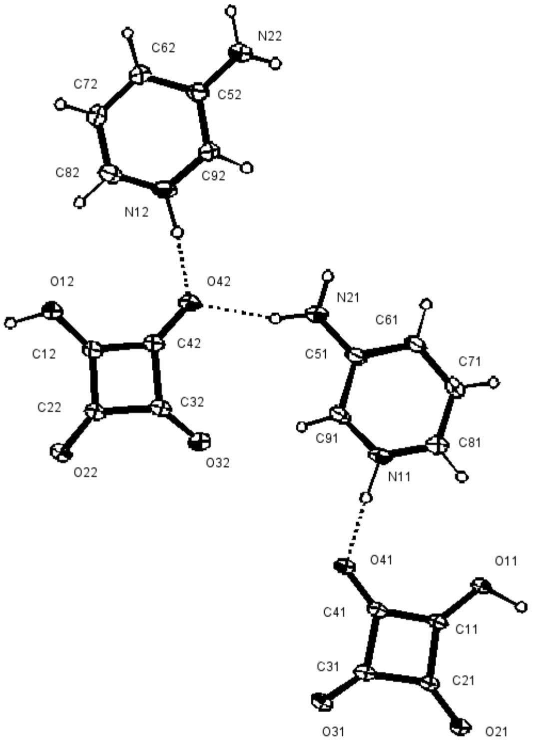


Figure 2
The molecular components of (2), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 3
Hydrogen-bonding parameters (Å, °).

	D—H	H···A	D···A	D—H···A
(1)				
O1—H1···O2$^{\mathrm{i}}$	0.94 (2)	1.58 (2)	2.498 (2)	163 (2)
N3—H32···O2	0.92 (2)	1.83 (2)	2.745 (2)	177 (2)
N1—H10···O3	0.94 (2)	1.88 (2)	2.796 (2)	165 (2)
N3—H31···N2$^{\mathrm{ii}}$	0.92 (2)	2.13 (2)	3.044 (2)	176 (2)
C7—H7···O4$^{\mathrm{iii}}$	0.92 (2)	2.33 (2)	3.215 (2)	159 (2)
C8—H8···O1$^{\mathrm{iv}}$	1.04 (2)	2.29 (2)	3.263 (2)	156 (2)
C6—H6···O3$^{\mathrm{iii}}$	1.00 (2)	2.38 (2)	3.311 (2)	154 (2)
(2)				
O12—H12···O22$^{\mathrm{v}}$	1.11 (4)	1.41 (4)	2.507 (3)	169 (4)
O11—H11···O21$^{\mathrm{vi}}$	0.90 (4)	1.63 (4)	2.514 (3)	166 (3)
N12—H120···O42	1.14 (7)	1.54 (7)	2.669 (3)	170 (6)
N11—H110···O41	1.11 (4)	1.60 (4)	2.682 (3)	165 (4)
N21—H212···O31$^{\mathrm{vii}}$	0.91 (4)	1.99 (4)	2.896 (4)	172 (4)
N22—H222···O32$^{\mathrm{vii}}$	0.88 (6)	2.06 (6)	2.932 (4)	175 (5)
N22—H222···O41$^{\mathrm{vii}}$	0.78 (4)	2.24 (4)	2.948 (4)	153 (4)
N21—H211···O42	0.93 (3)	2.05 (4)	2.929 (4)	157 (3)
C91—H91···O32	0.95 (3)	2.34 (3)	3.284 (4)	169 (3)
C92—H92···O31$^{\mathrm{vii}}$	0.89 (4)	2.42 (3)	3.290 (4)	165 (3)
C62—H62···O22$^{\mathrm{vii}}$	0.94 (4)	2.45 (4)	3.346 (4)	158 (3)
C61—H61···O21$^{\mathrm{vii}}$	0.97 (3)	2.42 (3)	3.359 (3)	164 (3)
C81—H81···O11	1.02 (4)	2.51 (4)	3.409 (4)	146 (3)
C82—H82···O12	1.03 (4)	2.65 (4)	3.441 (4)	133 (3)
(3)				
O1—H1···O2$^{\mathrm{viii}}$	0.93 (2)	1.59 (2)	2.504 (2)	164 (2)
N1—H10···O4	0.92 (2)	1.97 (2)	2.784 (2)	146 (2)
N2—H22···O3$^{\mathrm{ix}}$	0.92 (2)	1.95 (2)	2.871 (2)	175 (2)
N2—H21···O2$^{\mathrm{x}}$	0.85 (2)	2.11 (2)	2.918 (1)	161 (2)
C7—H7···O4$^{\mathrm{xi}}$	0.98 (2)	2.47 (2)	3.186 (2)	130 (1)
C7—H7···O1$^{\mathrm{xi}}$	0.98 (2)	2.50 (2)	3.301 (2)	139 (2)
C9—H9···O3$^{\mathrm{x}}$	0.95 (1)	2.48 (1)	3.400 (2)	161 (2)
(4)				
N1—H1···O1	0.97 (2)	1.66 (2)	2.627 (1)	174 (2)
N2—H21···O2$^{\mathrm{xii}}$	0.89 (2)	2.00 (2)	2.883 (1)	172 (1)
N2—H22···O1	0.91 (2)	2.04 (2)	2.917 (1)	161 (1)
C3—H3···O2	1.02 (1)	2.22 (1)	3.171 (1)	156 (1)

Symmetry codes: (i) $1-x, -y, -z$; (ii) $2-x, -y, 2-z$; (iii) $1-x, 1-y, 2-z$; (iv) $1+x, y, 2+z$; (v) $-x, -y, -z$; (vi) $2-x, -1-y, 1-z$; (vii) $1+x, 1+y, z$; (viii) $1-x, -y, 1-z$; (ix) $-x, -y, 2-z$; (x) $-x, y-1, \frac{3}{2}-z$; (xi) $1-x, -y, 2-z$; (xii) $x, y, z+1$.

standard reflections were measured every 2 h and did not show significant variations for all the compounds investigated. Intensities were corrected for Lorentz and polarization effects. Scattering factors were taken from *International Tables for X-ray Crystallography* (Cromer & Waber, 1974). The structures were solved by direct methods using the *SIR*92 (Altomare *et al.*, 1994) system of programs and refined by full-matrix least-squares with anisotropic non-H and isotropic H atoms using *SHELXL*97 (Sheldrick, 1997); all other calculations were accomplished using *PARST* (Nardelli, 1983, 1995) and *PLATON* (Spek, 1998). Selected bond distances are reported in Table 2 and hydrogen-bonding parameters in Table 3. *ORTEP*II (Johnson, 1976) views are shown in Figs. 1–4.

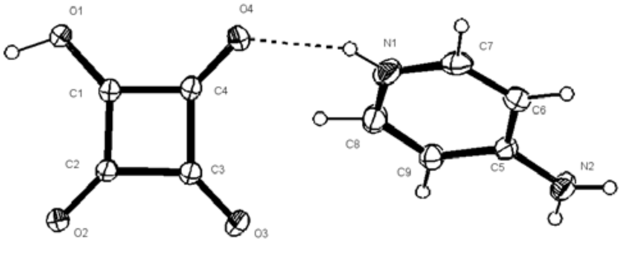


Figure 3
The molecular components of (3), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

3. Description of crystal packings

3.1. Structure (1): 2-aminopyrimidinium (2APMH$^+$) hydrogen squarate (HSQ$^-$)

The crystal consists of a three-dimensional van der Waals packing of two-dimensional planes which, in turn, are parallel associations of hydrogen-bonded ribbons held together by weak C—H···O interactions (Fig. 5). The ribbons are ladders whose rungs are alternated centrosymmetric dimers of HSQ$^-$

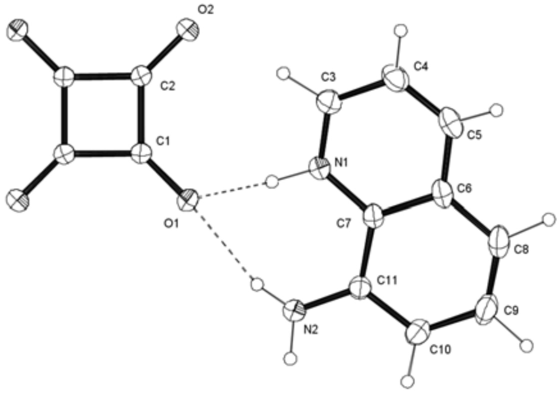


Figure 4
The molecular components of (4), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

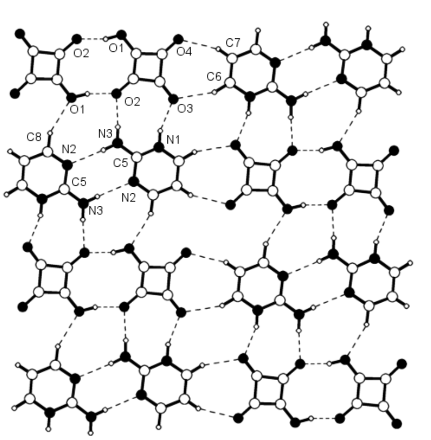
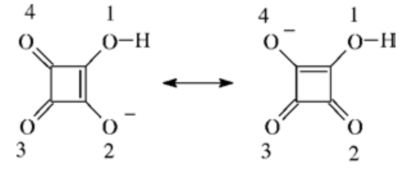


Figure 5
Layer of molecules of co-crystal (1) linked by hydrogen bonds.

and 2APMH$^+$ ions. The (HSQ$^-$)$_2$ dimer is linked by two strong negative-charge-assisted O1—H···O2$^{1/2-}$ bonds having a O···O distance of 2.498 (2) Å, which is at the upper limit of the range of 2.44–2.49 Å (Gilli *et al.*, 1994) observed in carboxylic acid–carboxylate complexes, most probably because of the weakening effects produced by the further hydrogen bonds accepted by O atoms. The 2APMH$^+$ dimer is held by two neutral N—H···N bonds [N2···N3 3.044 (2) Å] according to a motif which is a very well known supramolecular synthon (Etter & Desmond, 1990; Aakeröy *et al.*, 1998). The two different dimers are interconnected by two N1—H···O3 and N3—H···O2 bonds and one C—H···O interaction [C8···O1 3.263 (2) Å; H···O1 2.29 (2) Å], which is strictly comparable with the strongest C—H···O bonds found in Cl$_3$C—H···O [average H···O of 2.31 (1) Å] and —C≡C—H···O [average H···O of 2.40 (2) Å] interactions (Desiraju & Steiner, 1999). The N3—H···O2 bond is shorter [2.745 (2) Å] than N1—H···O3 [2.796 (2) Å], in spite of the fact that the formal positive charge is residing on the N1$^+$—H group and that positively charged hydrogen bonds are normally stronger. A reason for that is illustrated by the resonance (I*a*) ↔ (I*b*), for which the oxygen negative charge can never be on O3, being potentially shared only by the O2 and O4 atoms. The most energetically favoured N3$^+$—H···O2$^{1/2-}$ interaction is then achieved by moving the positive charge from N1 to N3, as clearly shown by the N3—C5 distance which is 1.312 (2) Å against the normal value of 1.34–1.35 Å in neutral 2APM (Furberg *et al.*, 1979; Scheinbeim & Schempp, 1976), and in touch with the same distance of 1.322 Å observed in the hydrochloride salt where the same transfer of charge to the ═NH$_2$$^+$ group occurs (Furberg & Grogaard, 1980).



(I*a*) (I*b*)

3.2. Structure (2): 3-aminopyridinium (3APH$^+$) hydrogen squarate (HSQ$^-$)

Also the crystal of (2) is a three-dimensional van der Waals packing of hydrogen-bonded planes (Fig. 6) and one of its structural motifs is the (HSQ$^-$)$_2$ dimer connected by O—H···O$^{1/2-}$ bonds of remarkable strength [2.510 Å as an average over two molecules of the asymmetric unit]. The inter-plane packing can be described in terms of ribbons of centrosymmetric (HSQ$^-$)$_2$ dimers interconnected with centrosymmetric 3APH$^+$ pairs through two N$^+$—H···O$^{1/2-}$ [N12···O42 2.669 (3) and N11···O41 2.682 (3) Å], two N—H···O═ [N21···O31 2.896 (4) and N22···O32 2.932 (4) Å] and six C—H···O [on average, C···O 3.39 (4) and H···O 2.51 (9) Å] hydrogen bonds. Both sides of the ribbon contain only hydrophilic groups, *i.e.* hydrogen-bond donor and acceptor atoms which become complementary when the adjacent ribbon is shifted upwards by one half of the distance between two (HSQ$^-$)$_2$ dimers. The resulting supramolecular architecture thus has two non-crystallographic glides perpendicular to its mean plane and approximately belongs to the plane group *pgg*. This symmetry is not retained by the three-dimensional crystal (space group $P\bar{1}$), which allocates the supramolecular symmetry in the form of a double asymmetric unit. The inter-ribbon connections are given by N—H···O bonds [N12···O42 2.669 (4) and N22···O41 2.948 (4) Å] and by C—H···O [C91···O32 3.284 (4); C92···O31 3.290 (4) Å], which are to be classified as relatively strong C—H···O bonds, in agreement with the acidic nature of the C atoms surrounded by two electronegative groups.

3.3. Structure (3): 4-aminopyridinium (4APH$^+$) hydrogen squarate (HSQ$^-$)

Crystals of (3) are not built up of van der Waals planes, but consist of a three-dimensional hydrogen-bonded structure,

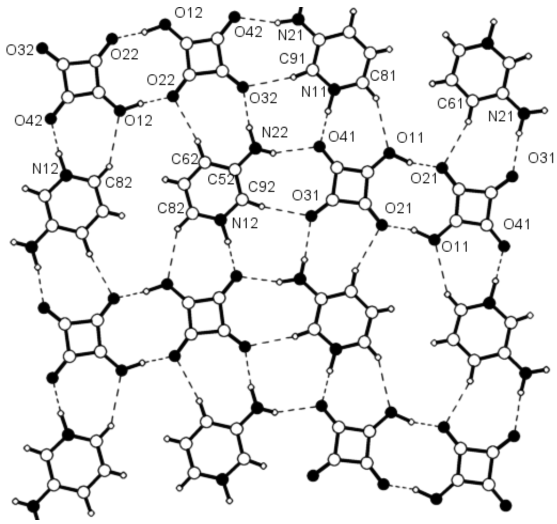


Figure 6
Layer of molecules of co-crystal (2) linked by hydrogen bonds.

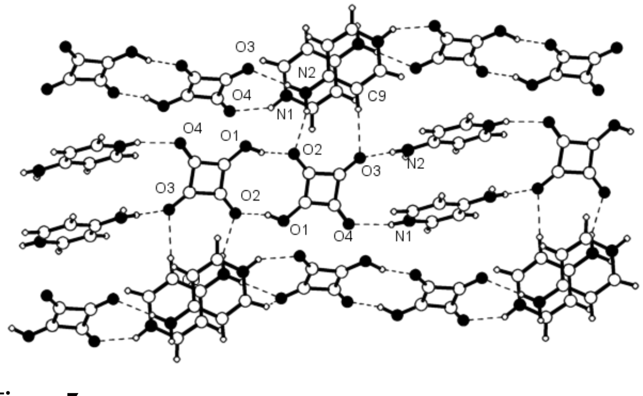


Figure 7
Three-dimensional arrangement of molecules of co-crystal (3) linked by hydrogen bonds.

Table 4
Saturation of potential hydrogen-bond donor and acceptor groups in the structures considered.

Hydrogen-bond donors (base pair or dimer)			Hydrogen-bond acceptors [$(HSQ^-)_2$ dimer or SQ^{2-} ion]		
Type	Potential	Used	Type	Potential	Used
(1)					
$N-H^+$	2	2	$O^{1/2-}$	12	10
N—H	2	2			
C—H	6	6			
(2)					
$N-H^+$	2	2	$O^{1/2-}$	12	12
N—H	4	4			
C—H	8	6			
(3)					
$N-H^+$	2	2	$O^{1/2-}$	12	12
N—H	4	4			
C—H	8	4†			
(4)					
$N-H^+$	2	2	$O^{1/2-}$	8	8
N—H	4	4			
C—H	12	2			

† Two bifurcated C—H···O bonds.

which can be described according to Fig. 7. Centrosymmetric $(HSQ^-)_2$ dimers linked by O—H···$O^{1/2-}$ bonds having O1···O2 2.504 (2) Å make horizontal chains with a non-bonded centrosymmetric pair of $4APH^+$ ions through N—H···O [N2···O3 2.871 (2) Å] and N^+—H···$O^{1/2-}$ [N1···O4 2.784 (2) Å] bonds. The chains are connected in a three-dimensional structure by N—H···O bonds between the second hydrogen of the aminic function and the O2 atom of the HSQ^- unit [N2···O2 2.918 (1) Å]. The N—H functions link the chains in planes nearly parallel to the plane of the drawing, while the $4APAH^+$ moieties nearly perpendicular to it connect the plane with other similar and parallel planes. The structure is complemented by rather short bifurcated C7—H···O1 and O4 [on average, C···O 3.24 and H···O 2.48 Å] and by C9—H···O3 [C···O 3.400 (2), H···O 2.48 (1) Å] interactions.

3.4. Structure (4): 8-aminoquinolinium ($8AQH^+$) hemisquarate (1/2 SQ^{2-})

The SQ^{2-} anions lie on centres of symmetry and the supramolecular architecture of this crystal is particularly simple. Each SQ^{2-} anion is surrounded by two centrosymmetric $8AQH^+$ cations, each one connected by two chelated N^+—H···$O^{1/2-}$ [N1···O1 2.627 (1) Å] and N—H···$O^{1/2-}$ [N2···O1 2.917 (1) Å] bonds and by one short C—H···O [C3···O2 3.171 (1) Å] interaction (Fig. 8). These three molecular units are linked in chains by N2—H···$O^{1/2-}$ bonds having a N···O distance of 2.833 (1) Å. The resulting ribbons are completely hydrophobic and pack together in a staggered pattern by van der Waals forces.

4. Discussion

In a previous paper (Bertolasi *et al.*, 2001) we have stressed the great difficulties that any prediction of co-crystal packing schemes may encounter even when the dominating molecular interactions are essentially known. The present structures make no exception to what was previously observed. Apart from the problem of *ab initio* prediction of the crystal packing by lattice energy calculations or molecular dynamics methods (which is far beyond the scope of the present paper), the simple understanding of the crystal supramolecular architectures appears to be out of the question for all structures except (4) and, perhaps, some aspects of (1). In (4) it could have been predicted that the presence of strong hydrogen-bond donors only on one side of the 8-aminoquinolinium ($8AQH^+$) cation would have produced the specular aggregation of two rows of $8AQH^+$ molecules around the same spine of squarate anions with the final formation of hydrophobic ribbons (Fig. 8). In (1) the previous knowledge that 2-aminopyrimidinium is liable to form a typical dimeric synthon could have induced us to forsee, as a plausible structural motif, the ribbon of alternating $(HSQ^-)_2$ and $(2APMH^+)_2$ dimers displayed in Fig. 5. Much more encouraging appear to be 'the degree of chemical understanding of the molecular interactions' (Bertolasi *et al.*, 2001) determining the packing itself. Table 3 reports all the D—H···A interactions (where D and A are the hydrogen-bond donor and acceptor atoms, respectively) found in co-crystals (1)–(4). These data can be rearranged in order of increasing $D···A$ distances, according to the following classes:

(*a*) —O—H···$O^{1/2-}$ in (1), (2) and (3) with 2.498 (2) ≤ d(O···O) ≤ 2.514 (5) Å;

(*b*1) ≡N^+—H···$O^{1/2-}$ in (2), (3) and (4) with 2.627 (1) ≤ d(N···O) ≤ 2.784 (2) Å;

(*b*2) ≡N^+(H)—H···$O^{1/2-}$ in (1) with d(N···O) 2.745 (2) Å;

(*b*3) —N(H)—H···O═ in (2) and (3) with 2.871 (1) ≤ d(N···O) ≤ 2.932 (4) Å;

(*b*4) —N(H)—H···$O^{1/2-}$ in (2), (3) and (4) with 2.883 (1) ≤ d(N···O) ≤ 2.929 (4) Å;

(*c*) ═N^+(H)—H···N≡ in (1) with d(N···N) = 3.044 (2) Å;

(*d*1) ≡C—H···$O^{1/2-}$ in (1), (2), (3) and (4) with 3.171 (1) ≤ d(C···O) ≤ 3.359 (2) Å;

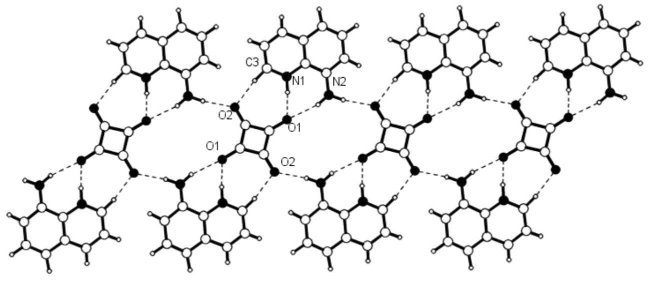


Figure 8
Ribbon of molecules of co-crystal (4) linked by hydrogen bonds.

(*d*2) $\equiv$C—H$\cdots$O in (1), (2) and (3) with $3.263\,(1) \leq d(\mathrm{C}\cdots\mathrm{O}) \leq 3.441\,(2)$ Å,

where the positive and negative charges reported are to be taken as purely formal. The shortest $D\cdots A$ distances belong to the negative-charge-assisted (−)CAHB class of [O—H$\cdots$O]$^-$ bonds, for which $d(\mathrm{O}\cdots\mathrm{O})$ values of 2.39–2.49 Å have already been reported (Gilli *et al.*, 1994; Bertolasi *et al.*, 1996). Values presently observed are on the longer-distance side of the distribution; this is to be imputed to the fact that the formal charge here is 1/2− or better, to an indirect weakening produced by further hydrogen bonds accepted by the two O atoms from the crystalline environment. Some interesting regularities are also observed for the N—H$\cdots$O bonds [classes (*b*1)–(*b*4)]. Bonds where the nitrogen and the oxygen bear opposite charges [classes (*b*1) and (*b*2)] are remarkably stronger than those where the N—H group is uncharged, in agreement with anything previously found for a much larger series of N—H$\cdots$O bonds (Gilli & Gilli, 2000). N—H$\cdots$N [class (*c*)] and C—H$\cdots$O [class (*d*)] are, as expected in view of the lower electronegativities of the atoms involved, increasingly weaker although, as remarked above, all C—H$\cdots$O presently observed are actually to be considered strong within their class of bonds, in view of the higher acidities of the C—H groups in nitrogen bases.

Table 4 summarizes the donor–acceptor properties of the hydrogen bonds observed in (1)–(4), taking as constitutive units of the crystal the centrosymmetric $(\mathrm{HSQ}^-)_2$ dimer or the SQ^{2-} ion [for structures (1)–(3) and (4), respectively] and the adjacent centrosymmetric pair of nitrogen bases, irrespective of whether or not they are linked in hydrogen-bond dimers [which actually happens only for (1); see Fig. 5]. Since $\mathrm{H_2SQ}$ is a flat and π-delocalized molecule, the four O atoms of its anions can be considered sp^2 electron donors. In this hypothesis the $(\mathrm{HSQ}^-)_2$ dimer and SQ^{2-} ion are possible acceptors of 12 and eight hydrogen bonds, respectively. The data of Table 4 indicate that all these acceptor positions are systematically matched by hydrogen-bond donors following a rather precise energy rule, in the sense that the packing is chosen in such a way to realise firstly the strongest possible bonds, *i.e.* O—H$\cdots$O$^{1/2\,-}$, N—$^+$H$\cdots$O$^{1/2-}$ and N—H$\cdots$O for which all possible donor groups turns out to be fully utilized. The remaining acceptors are then totally saturated through weaker C—H$\cdots$O interactions.

The observed behaviour suggests some considerations of quite general character on the process of crystal packing of hydrogen-bonded molecular crystals. It has been sometimes stated (Donohue, 1952; Etter, 1991) that the main rule for hydrogen-bonded crystals is that '*all acidic H atoms available in a molecule will be used in hydrogen bonding in the crystal structure of that compound*' (of course, if there are acceptors). This rule also holds for the present set of data (Table 4) provided that C—H$\cdots$O interactions are not considered to be hydrogen bonds. If these are considered, it seems more reasonable to rewrite the rule as: **Rule 1**: 'All the hydrogen-bond acceptors available in a molecule will be engaged in hydrogen bonding as far as there are available donors' and to complement it by the useful auxiliary rule that is: **Rule 2**: 'The hydrogen-bond acceptors will be saturated in order of decreasing strength of the hydrogen-bond formed'. This second rule tells us that since C—H$\cdots$O and C—H$\cdots$N are usually the weakest bonds, the crystal hydrogen-bond pattern will normally be completed by the maximum number of these weaker interactions. Notice that Rule 1 is in agreement with previous remarks by Taylor & Kennard (1984) that one of the factors determining the hydrogen-bond arrangements is 'a preference for including as many acceptors as possible in the hydrogen-bonding scheme'.

Much could be said on the validity of Rules 1 and 2 and on their transferability from the limited dataset of Table 4 to the crystal packings of all molecular crystals consisting of potentially hydrogen-bonding molecules. The two rules can be considered to hold in general on condition that the hydrogen bonds formed do not become too weak, and the present data seem to indicate that C—H$\cdots$O bonds can easily satisfy this condition when, as in the present case, all C—H groups involved in hydrogen-bond formation have some extra acidic character due to both the aromatic nature of the ring and the presence of electronegative adjacent N atoms. It may be of interest to remark that the principle of saturation of all acceptors by hydrogen-bond donors down to acidic C—H groups has previously called upon to explain the higher bioactivity of drugs endowed with a number of functional groups able to enhance C—H acidity (Bertolasi *et al.*, 1990; Saenger, 1973; Jeffrey & Maluszynska, 1982).

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