Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Associations of squaric acid and its anions as multiform building blocks of hydrogen-bonded molecular crystals

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Received 26 June 2001
Accepted 12 September 2001

Squaric acid, $H_2C_4O_4$ (H_2SQ), is a completely flat diprotic acid that can crystallize as such, as well as in three different anionic forms, *i.e.* $H_2SQ{\cdot}HSQ^-$, HSQ^- and SQ^{2-}. Its interest for crystal engineering studies arises from three notable factors: (i) its ability of donating and accepting hydrogen bonds strictly confined to the molecular plane; (ii) the remarkable strength of the $O-H\cdots O$ bonds it may form with itself which are either of resonance-assisted (RAHB) or negative-charge-assisted [(−)CAHB] types; (iii) the ease with which it may donate a proton to an aromatic base which, in turn, back-links to the anion by strong low-barrier $N-H^+\cdots O^{1/2-}$ charge-assisted hydrogen bonds. Analysis of all the structures so far known shows that, while H_2SQ can only crystallize in an extended RAHB-linked planar arrangement and SQ^{2-} tends to behave much as a monomeric dianion, the monoanion HSQ^- displays a number of different supramolecular patterns that are classifiable as *β-chains*, *α-chains*, *α-dimers* and *α-tetramers*. Partial protonation of these motifs leads to $H_2SQ{\cdot}HSQ^-$ anions whose supramolecular patterns include *ribbons of dimerized β-chains* and *chains of emiprotonated α-dimers.* The topological similarities between the three-dimensional crystal chemistry of orthosilicic acid, H_4SiO_4, and the two-dimensional one of squaric acid, $H_2C_4O_4$, are finally stressed.

1. Introduction

Squaric acid is a strong biprotic acid that can crystallize as pure H_2SQ (Semmingsen *et al.*, 1977; Gilli & Bertolasi, 1990) as well as hydrogen squarate (HSQ^-) or squarate (SQ^{2-}) anions, the last two being particularly suited for interacting with a variety of hydrogen-bond donors. H_2SQ and its anions are almost perfectly flat molecules in view of the π-conjugation of their C—C and C—O bonds, and, because of that, their four O atoms behave as planar (sp^2) electron donors of one or two lone pairs (Bertolasi *et al.*, 2001). Resonance is known to stabilize the monoanion (II) (Fig. 1) and, at a greater extent, the dianion (III) with respect to the indissociated acid (I). This increased stabilization accounts for the fact that both H_2SQ and HSQ^- are remarkably strong acids (pK_1 = 1.2–1.7; pK_2 = 3.2–3.5; Ireland & Walton, 1967; MacDonald, 1968) with a small difference between the two dissociation constants.

In the last years squaric acid and its anions have been frequently used as counteranions in the preparation of a number of molecular crystals. A search on the CSD (release October 2000; Allen *et al.*, 1979) has given, besides the structure of squaric acid (Semmingsen *et al.*, 1977), 24 and 25 other structures of crystals containing the HSQ^- and SQ^{2-} anions, respectively. Therefore, we are now providing a first account on the crystal chemistry of these ions and on their ability of organizing, in specific predictable ways, the structures of the molecular crystals they are embedded in. Data collected shows that while H_2SQ can crystallize in a unique planar arrangement and SQ^{2-} behaves much as a monomeric dianion, the monoanion HSQ^- may display a considerable number of polyanionic supramolecular architectures which are the main subject of the present paper. Figs. 2 and 3 sketch the types of polymeric patterns formed by H_2SQ and HSQ^- in their crystals, while Fig. 4 reports the mean geometries of the C_4O_4 frame for these different typologies. Figs. 5–10 display a number of actual crystal structures which seem particularly suited for illustrating the specific packing of each arrangement. A summary of the topological aspects of the different patterns encountered is finally reported in Fig. 11.

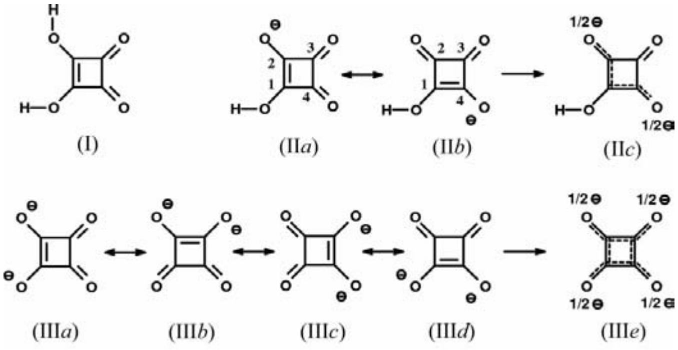


Figure 1
VB forms of H_2SQ (I), HSQ^- (II) and SQ^{2-} (III) showing the increased stabilization by resonance with the increasing negative charge.

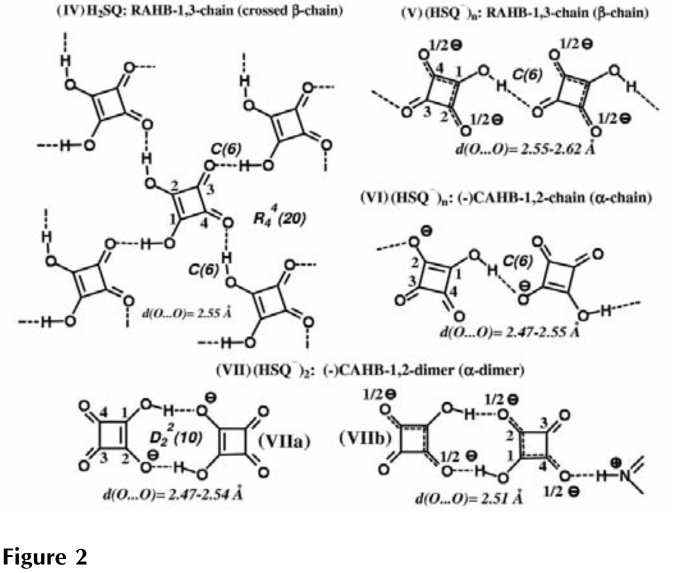


Figure 2
The hydrogen-bonded supramolecular patterns found in crystals of H_2SQ and its HSQ^- anion: (IV) double-resonant β-chain formed by H_2SQ (KECYBU06: Semmingsen *et al.*, 1977); (V) resonant β-chain formed by HSQ^- (CELCEB: Endres & Schendzielorz, 1984; FEGLUY and FEGMAF: Brach *et al.*, 1987; NUYFUI: Kolev *et al.*, 1998); (VI) [O—H$\cdots$O]$^-$ α-chain formed by HSQ^- (HIVQEI: Kolev *et al.*, 1999; KHSQR: Bull *et al.*, 1973; PIQTIS: Kolev, Stahl *et al.*, 1997; SADQUJ: Braga & Grepioni, 1998; TEHYUA: Angelova *et al.*, 1996; TIWWUR: Karle *et al.*, 1996); (VII*a*) the [O—H$\cdots$O]$^-$ α-dimer formed by HSQ^- (BOLFUD: Bock *et al.*, 1998; BOQDUG: MacLean *et al.*, 1999; KINKEX: Kanters *et al.*, 1991; TIDCAK: Angelova *et al.*, 1996; TIWXIG: Karle *et al.*, 1996; Bertolasi *et al.*, 2001). (VII*b*) The 'perturbed' [O—H$\cdots$O]$^-$ α-dimer formed by HSQ^- (Bertolasi *et al.*, 2001).

2. Results and discussion

All the polymeric patterns displayed in Figs. 2 and 3 are built up of H_2SQ (IV) and HSQ^- (V)–(VIII) units, or by (IX)–(X) connected by a net of O—H$\cdots$O bonds whose $d(O\cdots O)$ distances, or range of distances, in Å are displayed in italics on the figures in association with each pattern, together with hydrogen-bond symbology (Etter *et al.*, 1990; Bernstein *et al.*, 1995). All O—H$\cdots$O bonds are remarkably short and presumably strong, laying in the range $2.43 \leq d(O\cdots O) \leq 2.56$ Å, which corresponds to a range of hydrogen-bond energies of $38 \leq E_{HB} \leq 84$ kJ mol^{-1} according to the Lippincott & Schroeder (1955) force field. They are therefore definitely stronger than ordinary O—H$\cdots$O bonds, such as those connecting the water molecules in ice [$d(O\cdots O)$ = 2.74 Å; $E_{HB} \simeq 17$ kJ mol^{-1}] .

Strong homonuclear O—H$\cdots$O bonds have been fully classified by Gilli *et al.* (1994) who were able to show, on the grounds of large neutron and X-ray crystal-structure evidence, that there are but three classes of really strong (short) O—H$\cdots$O bonds:

(i) (−)CAHBs: [O—H$\cdots$O]$^-$ negative-charge-assisted hydrogen bonds [$2.38 \leq d(O\cdots O) \leq 2.50$ Å];

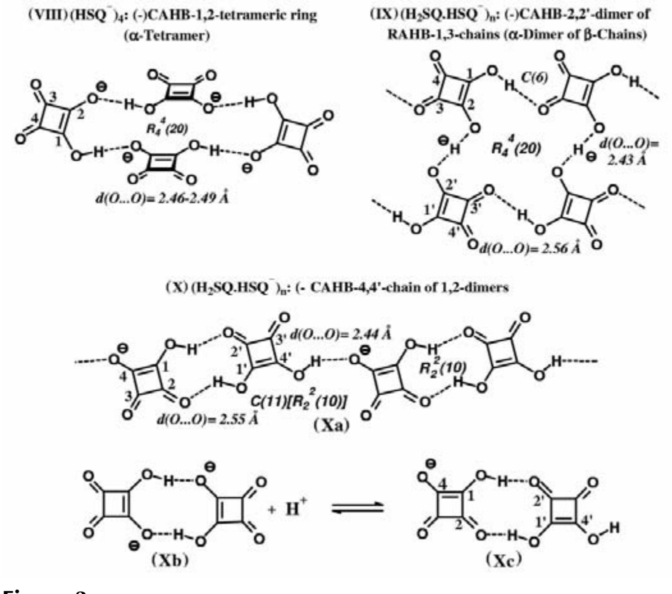
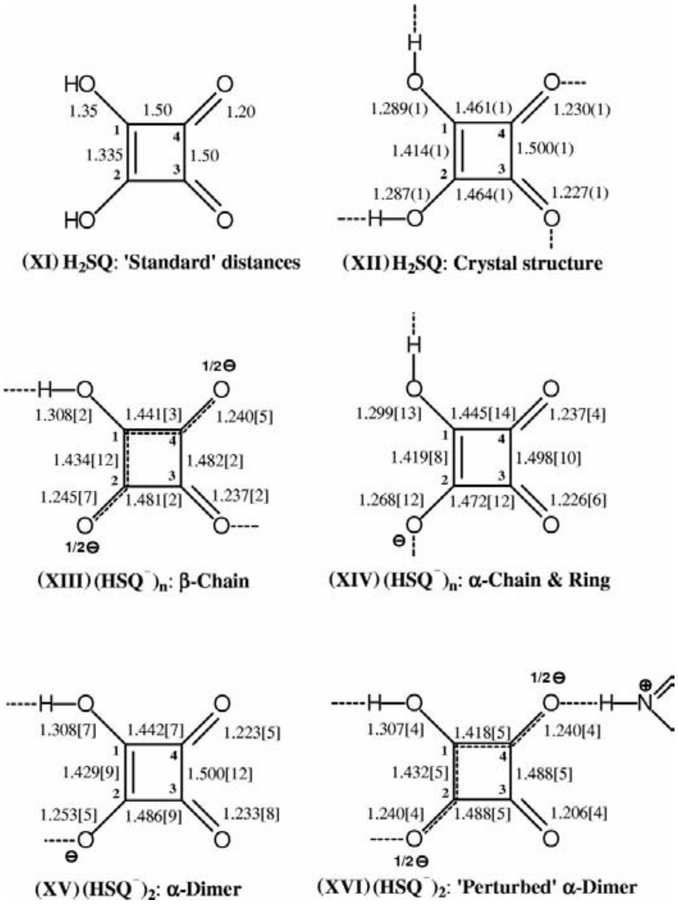


Figure 3
Another hydrogen-bonded supramolecular pattern formed by the HSQ^- anion: (VIII) the [O—H$\cdots$O]$^-$ α-tetramer (RAVWAM: Kolev, Preut *et al.*, 1997). The hydrogen-bonded supramolecular patterns formed in crystals by the $H_2SQ\cdot HSQ^-$ anion: (IX) two resonant β-chains interconnected by [O—H$\cdots$O]$^-$ bonds (Lin *et al.*, 1994); (X*a*) [O—H$\cdots$O]$^-$ α-chain of $H_2SQ\cdot HSQ^-$ dimers (SADRAQ: Braga & Grepioni, 1998); (X*b*,*c*) protonation of the [O—H$\cdots$O]$^-$ α-dimer (X*b*) with formation of the ($H_2SQ\cdot HSQ^-$) anion (X*c*).

(ii) (+)CAHBs: $[\mathrm{O-H\cdots O}]^+$ positive-charge-assisted hydrogen bonds $[2.36 \leq d(\mathrm{O\cdots O}) \leq 2.43\ \text{Å}]$;

(iii) RAHBs: $-\mathrm{O-H\cdots O}{=}$, resonance-assisted hydrogen bonds where the two O atoms are connected by a π-conjugated system of single and double bonds $[2.39 \leq d(\mathrm{O\cdots O}) \leq 2.55\ \text{Å}]$.



(XI) H_2SQ: 'Standard' distances

(XII) H_2SQ: Crystal structure

(XIII) $(HSQ^-)_n$: β-Chain

(XIV) $(HSQ^-)_n$: α-Chain & Ring

(XV) $(HSQ^-)_2$: α-Dimer

(XVI) $(HSQ^-)_2$: 'Perturbed' α-Dimer

Figure 4
Average crystallographic bond distances in H_2SQ and its HSQ^- anions, whose supramolecular patterns are reported in (IV)–(VII) of Fig. 2. The e.s.d's are given in parentheses and e.s.d's from the mean in square brackets. (XI) reports the 'standard' bond distance of H_2SQ unperturbed by π-delocalization and hydrogen-bond formation (Gilli *et al.*, 1993).

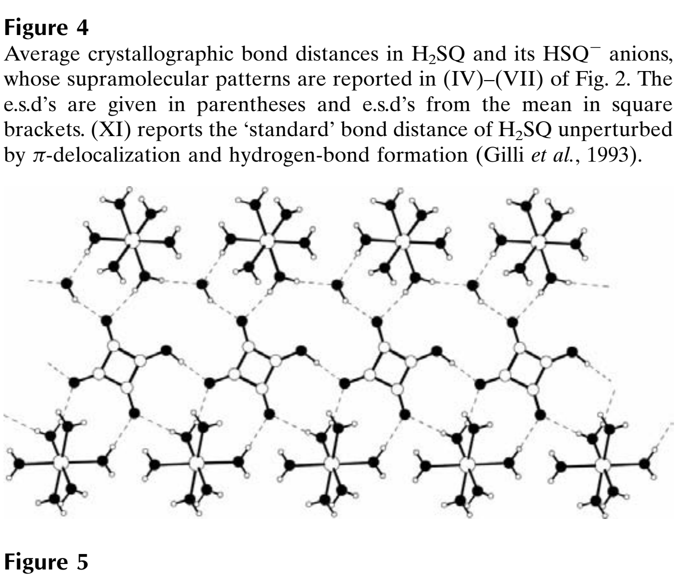


Figure 5
β-chain of HSQ^- anions surrounded by hydrogen-bonded water molecules free or coordinated in hexa-aquo cobalt anions (FEGMAF: Brach *et al.*, 1987).

Typical (−)CAHBs are the intermolecular $R\mathrm{COOH}\cdots{}^-\mathrm{OOC}R$ bonds in carboxylic acid–carboxylate complexes, (+)CAHBs those formed by two oxygenated molecules ($\mathrm{H_2O\cdots H^+\cdots OH_2}$, $R_2\mathrm{O\cdots H^+\cdots O}R_2$, $\mathrm{Me_2S{=}O\cdots H^+\cdots O{=}SMe_2}$ *etc.*) bridged by a proton donated by a strong acid within the crystal, while the most common cases of RAHB are the strong $-\mathrm{O-H\cdots O}{=}$ bonds formed by the heteroconjugated $\cdots\mathrm{O{=}C-C{=}C-OH}\cdots$$\beta$-diketone enol group.

Simple inspection of Figs. 2 and 3 shows that all the $\mathrm{O-H\cdots O}$ bonds formed by H_2SQ and HSQ^- belong to two out of these three classes of strong bonds, *i.e.* (−)CAHB and RAHB, whose different expressions give rise to the variety of association patterns (IV)–(X) individually described in some detail in the following sections.

2.1. β-Chains: RAHB 1,3-chains (IV) and (V)

β-Diketone (or 1,3-diketone) enols $\cdots\mathrm{O{=}C-C{=}C-OH}\cdots$ make normally strong intramolecular RAHBs by closing a hydrogen-bonded six-membered ring. When this is forbidden for steric reasons (*e.g.* in 1,3-cyclopentandione or

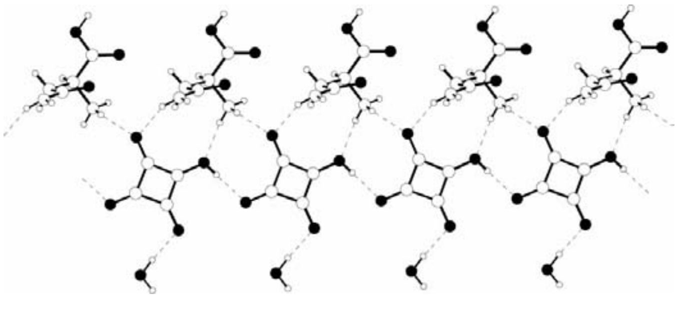


Figure 6
β-chain of HSQ^- anions surrounded by hydrogen-bonded water molecules and asparaginium cations (NUYFUI: Kolev *et al.*, 1998).

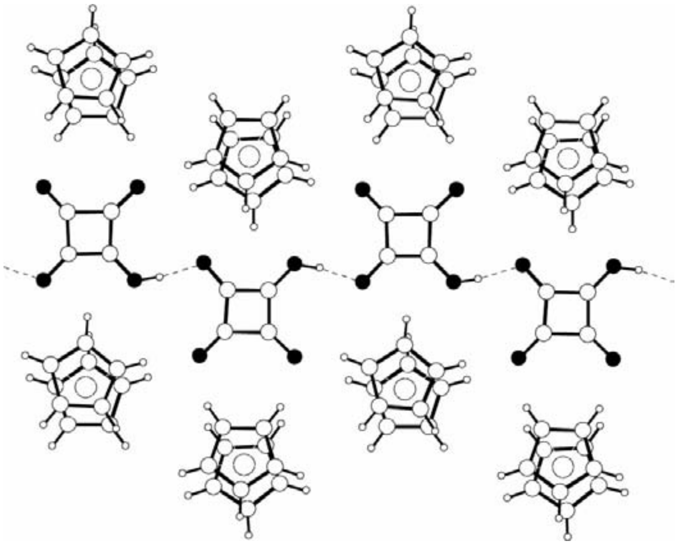


Figure 7
Isolated α-chain of HSQ^- anions surrounded by cobaltocenium cations (SADQUJ: Braga & Grepioni, 1998).

1,3-cyclohexandione enols) molecules crystallize by forming extended RAHB chains (resonant β-chains; Gilli *et al.*, 1993; Bertolasi *et al.*, 1996).

The molecule of H_2SQ (I) consists of two β-diketone enol groups intercrossed along the square diagonals. Accordingly, it crystallizes by making planes of two intersecting β-chain systems (IV) characterized by short $O-H\cdots O$ RAHBs having $d(O\cdots O) = 2.554$ (1) Å and by the typical perturbation of the C—C and C—O bonds shown in (XII) of Fig. 4 (see for a detailed discussion Gilli *et al.*, 1993).

Deprotonated HSQ^- can still make one $(HSQ^-)_n$ β-chain (V), which is actually the superimposition on the same track of two RAHB chains, *i.e.* $\cdots O{=}C3-C2{=}C1-OH\cdots$ and $\cdots O{=}C3-C4{=}C1-OH\cdots$, with the consequent symmetrization of the C_4O_4 fragment around the $C1\cdots C3$ diagonal shown in (XIII) and with the formation of an $O-H\cdots O$ RAHB of a length strictly comparable to that of H_2SQ [$d(O\cdots O)$ of 2.55–2.62 Å against 2.55 Å]. Since the HSQ^- negative charges are not used in β-chain formation, these negative charges remain confined over the O2 and O4 atoms at the borderline of the $(HSQ^-)_n$ chain with formal charges of $\frac{1}{2}-$. Accordingly, the β-chain is strongly hydrophilic and it is found, in crystals, to be totally surrounded by water molecules (*e.g.* FEGMAF: Brach *et al.*, 1987; Fig. 5) or by both water and protonated amines or aminoacids (*e.g.* NUYFUI: Kolev *et al.*, 1998; Fig. 6).

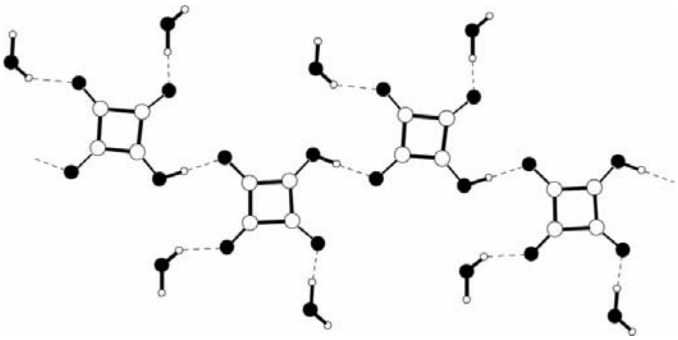


Figure 8
α-chain of HSQ^- anions surrounded by hydrogen-bonded water molecules (KHSQUR: Bull *et al.*, 1973).

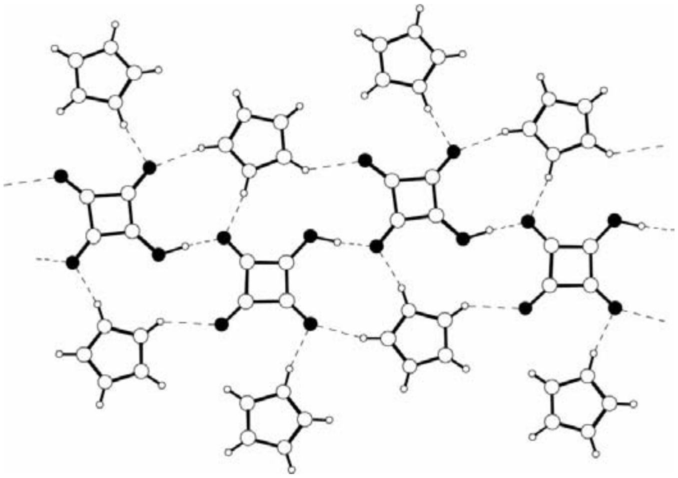


Figure 9
α-chain of HSQ^- anions surrounded by hydrogen-bonded imidazolium cations (TIWWUR: Karle *et al.*, 1996).

2.2. α-Chains: (−)CAHB-1,2 chains (VI)

Besides the β-diketone enol group that may form β-chains, the HSQ^- ion contains a further $^-O-C2{=}C1-OH$ α-diketone enolate (or 1,2-diketone enolate) group suitable for forming $[O-H\cdots O]^-$ (−)CAHBs, which are even stronger

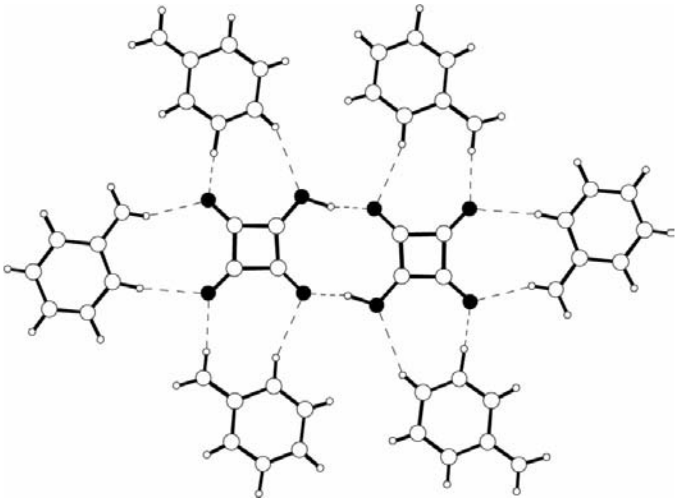


Figure 10
α-dimer of HSQ^- anions surrounded by hydrogen-bonded 3-aminopyridinium cations (Bertolasi *et al.*, 2001).

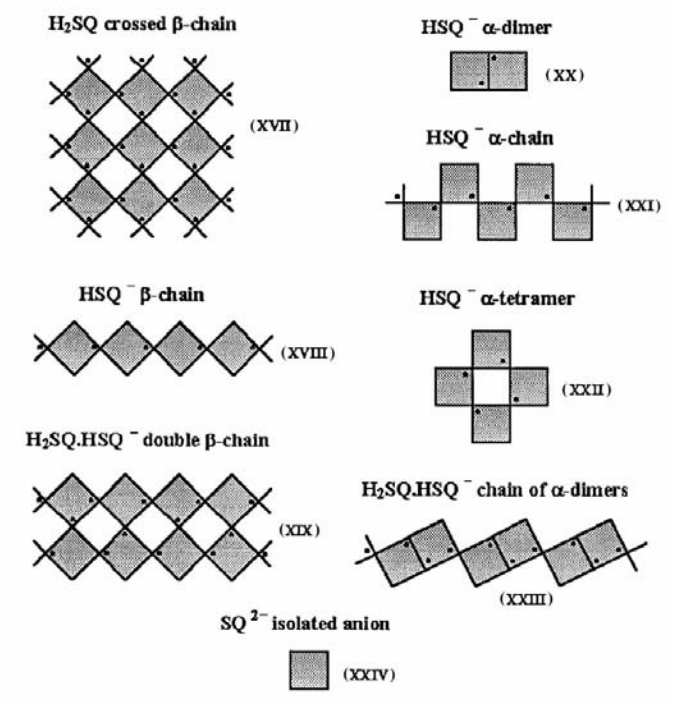


Figure 11
Schemes of the polymeric structures formed by squaric acid and its anions in crystals. The C_4O_4 frame is represented as a square and the hydroxyl positions by dots.

than RAHBs. It can form a second type of chain, the (−)CAHB-1,2 chain or α-chain (VI) linked by $[O{-}H\cdots O]^-$ bonds having $O\cdots O$ distances in the range 2.47–2.55 Å, slightly longer than the standard range of 2.38–2.50 Å reported for isolated (−)CAHBs, where the two O atoms do not accept other hydrogen bonds from the environment (Gilli *et al.*, 1994). In α-chains the negative charges are localized on the chain itself, in particular on the $[C1{-}OH\cdots O{-}C2]^-$ bridge, and not delocalized over the chain–environment borderline as in β-chains. Accordingly, α-chains are less hydrophilic than β-chains and can also occur in non-solvated environments, such as the isolated α-chain of cobaltocenium·HSQ^- (SADQUJ: Braga & Grepioni, 1998) displayed in Fig. 7, although the cases where the external O atoms are saturated by hydrogen-bond donors [water molecules in KHSQUR: Bull *et al.*, 1973 (Fig. 8); protonated amines in TIWWUR: Karle *et al.*, 1996 (Fig. 9) or both, *e.g.* HIVQEI: Kolev *et al.*, 1999] are more common.

2.3. *α*-Dimers: (−)CAHB-1,2 dimers (VII)

The formation of α-dimers (VII) is one of the most common ways of aggregation of HSQ^- anions which are now linked by two strong $[O{-}H\cdots O]^-$ (−)CAHBs. The observed range of $O\cdots O$ distances of 2.47–2.54 Å is very similar to that found in α-chains, although the $O{-}H\cdots O$ bonds in the latter are normally more linear.

As a crystal structural unit (tecton) the α-dimer can sometimes crystallize as an isolated anion (SADRAQ: Braga & Grepioni, 1998; BOQDUG: MacLean *et al.*, 1999), but normally behaves as a planar 12-lone-pair hydrogen-bond acceptor particularly suited to form co-crystals (mixed crystals) with mostly aromatic nitrogen amines protonated by the dissociation of the squaric acid itself. The structures formed are most frequently planar (*e.g.* Fig. 10; Bertolasi *et al.*, 2001), although a few cases of three-dimensional associations are also known (Bertolasi *et al.*, 2001; Karle *et al.*, 1996). All structures containing α-dimers share the interesting property of being completely anhydrous, in spite of the fact that most of them were crystallized from water. As hydrogen-bond acceptors, the four O atoms of the HSQ^- subunit display different behaviours. The carbonylic O3 atom is only found to be an acceptor of rather weak and neutral $N{-}H\cdots O3$ bonds, while positively charged hydrogen-bond donors tend to bind to the O2 and O4 atoms. The reason is seen in the resonance schemes (II) (Fig. 1), showing that only these two last atoms are charged and may then form $N^+{-}H\cdots O^{1/2-}$ or $N^+{-}H\cdots O^-$ bonds.

2.4. *α*-Dimer relaxation under the external hydrogen-bond field

In the last few years increasing attention has been devoted to hydrogen bonds which can be related to the acid–base equilibrium

$$AcO{-}H\cdots N{\equiv} \rightleftharpoons AcO^-\cdots H{-}N^+{\equiv} \qquad (1)$$

where $N{\equiv}$ is a nitrogen base, most frequently aromatic, and AcOH can be an organic (carboxylic acid, phenol, squaric acid) as well as an inorganic acid. It is now generally recognized that:

(i) the proton position ($O{-}H\cdots N$ or $O^-\cdots H{-}N^+$) is essentially determined by the difference of the gas-phase proton affinities, ΔPA, or, alternatively, by the corresponding ΔpK_a in aqueous solution;

(ii) very strong $N{-}H\cdots O$ bonds (up to 85–105 kJ mol^{-1}) must be associated with the condition ΔPA, or ΔpK_a, approaching zero (Malarski *et al.*, 1982; Zeegers-Huyskens, 1991; Sobczyk, 1998; Reinhardt *et al.*, 1998).

These very strong bonds with almost perfect pK_a matching have been given, particularly in the biochemical literature, the name of low-barrier hydrogen bonds (LBHBs) and are supposed to play an important role in some processes of enzymatic catalysis (Cleland, 1992; Cleland & Kreevoy, 1994; Frey *et al.*, 1994). More recently, all hydrogen bonds derived from equilibrium (1) have been given the alternative name (+/−)CAHB (positive/negative charge-assisted hydrogen bond; Gilli & Gilli, 2000) in analogy with the already established (+)CAHB, (−)CAHB and RAHB nomenclature (Gilli *et al.*, 1994).

As discussed above, the $(HSQ^-)_2$ α-dimer can be an acceptor of (+/−)CAHB formed by the partially charged O2 and O4 atoms with protonated nitrogen bases, whose strength is modulated by the ΔpK_a of the interacting moieties. Most of these bonds are only moderately strong, being in the $N\cdots O$ range 2.72–2.78 Å (Bertolasi *et al.*, 2001; Karle *et al.*, 1996; Endres & Schendzielorz, 1984), and are found in association with the average geometry of the C_4O_4 frame displayed in (XV) (Fig. 4). This is characterized, in analogy with that found for α-chains (XIV), by a strong bond dissymmetry around the HO1C1C3O3 diagonal, in particular as far as the $C2{-}O2$ and $C4{-}O4$ distances [on average, 1.253 (5) and 1.223 (5) Å in (XV) and 1.268 (12) and 1.237 (4) Å in (XIV)] are concerned, in agreement with the idea that the $[O1{-}H\cdots O2]^-$ bond shifts the tautomeric equilibrium (II) (Fig. 1) towards the form (II*a*).

Rather surprisingly, the formation of a single stronger $\equiv N^+{-}H\cdots O4$ bond having $d(N\cdots O)$ of 2.675 (6) Å (Fig. 10; Bertolasi *et al.*, 2001) seems able to upset such a bonding situation by changing the molecular symmetry from (VII*a*) to (VII*b*) (Fig. 2) and the bond distances from (XV) to (XVI) (Fig. 4). The new geometry is now almost perfectly diagonal-symmetric with $d(C2{-}O2) = d(C4{-}O4) = 1.240\,(4)$ Å and $d(C2{-}C3) = d(C3{-}C4) = 1.488\,(5)$ Å, on average, with bond distance shifts that can reach 0.027 Å. The most straightforward reason for this fact seems to be that the pK_a (6.0) of the aminopyridinium ion (Fig. 10) better matches the unknown pK_a of the $(HSQ^-)_2$ α-dimer to form a very strong $N^+{-}H\cdots O4^-$ LBHB. This, in turn, causes a withdrawal of electrons towards O4 and from the α-dimer, which thus changes its ground state from mainly (II*a*) (Fig. 1) to an almost perfect mixture of (II*a*) and (II*b*), *i.e.* to (II*c*), with final equal sharing of the negative charge between the O2 and O4 atoms.

Since symmetrical arrangements can only be energy minima or maxima in the molecular configuration space, it seems reasonable to assume that the diagonal-symmetric geometry (VII*b*)/(XVI) marks the geometry of the transition state (TS) along the protonation reaction pathways

$$(\mathrm{X}b) \rightleftharpoons TS \rightleftharpoons (\mathrm{X}c) \qquad (2)$$

connecting the two dissymmetric lower-energy states (X*b*) and (X*c*) (Fig. 3).

2.5. More complex HSQ^- and $H_2SQ{\cdot}HSQ^-$ polyanions

β-Chains (V), α-chains (VI) and α-dimers (VII) can be considered the normal aggregation forms of the HSQ^- anion. This anion can, however, associate in other more complex forms that, so far, have not been observed more than once, but that seem to open new interesting perspectives in the design of new squaric acid-based co-crystals.

The simplest case is represented by the $(HSQ^-)_4$ (−)CAHB-1,2 tetrameric ring [or α-tetramer (VIII); RAVWAM: Kolev, Preut *et al.*, 1997], whose O—H···O bonds [$2.46 \le d(\mathrm{O}\cdots\mathrm{O}) \le 2.49$ Å] and C_4O_4 frame geometries are very similar to those for α-chains (VI)/(XIV).

More interestingly, the case described in (IX) (Lin *et al.*, 1994) consists of two parallel and antidromic β-chains, where the monomers are linked by 1,3-RAHBs with $d(\mathrm{O}\cdots\mathrm{O})$ = 2.564 (1) Å [strictly similar to those found in H_2SQ (IV) and β-chains (V)] transversally connected in pairs by very short and perfectly centered $[\mathrm{O}\cdots\mathrm{H}\cdots\mathrm{O}]^-$ (−)CAHBs with $d(\mathrm{O}\cdots\mathrm{O})$ = 2.432 (1) Å. Note that the pattern of (IX) is no longer a polyanion of HSQ^-, but of the $H_2SQ{\cdot}HSQ^-$ dimeric anion, having acquired a single proton for each pair of HSQ^- anions.

A similar change of protonation state occurs in (X) (SADRAQ; Braga & Grepioni, 1998; Fig. 3) which can be classified as a (−)CAHB-4,4′ chain of α-dimers protonated at the O4′ positions according to the equilibrium

$$(\mathrm{HSQ}^-)_2 + \mathrm{H}^+ \rightleftharpoons \mathrm{H_2SQ}\cdot\mathrm{HSQ}^-$$

displayed in (X*b*,*c*).

3. Conclusions: crystal chemistry of squaric acid and its anions

The crystal chemistry of squaric acid appears to be rather more complicated than its solution chemistry. In water H_2SQ behaves as a strong diprotic acid with the formation of both HSQ^- and SQ^{2-} anions. In crystals, however, the HSQ^- anion exists in at least four different forms: β-chain (V), α-chain (VI), α-dimer (VII) and the α-tetramer (VIII). Moreover, in the crystal environment, a third acid anion appears with the same $H_2SQ{\cdot}HSQ^-$ formula but with two completely different geometries, the first corresponding to the chain of 4′-protonated α-dimers displayed in (X*a*), and the second to the 1:1 complex of two β-chains linked in ribbons by very strong 2–2′-(−)CAHBs shown in (IX).

The various manifestations of squaric acid in crystals cannot, therefore, be explained in terms of the simple chemical classification of its anions, in strict analogy with what happens in the crystal chemistry of silicates, a class of compounds with which squaric acid derivatives seem to have not irrelevant affinities. Squaric acid, $H_2C_4O_4$, has in fact definite topological similarities with the orthosilic acid, H_4SiO_4, consisting of a core (the C_4 frame or the Si atom) connectable to other nuclei by up to four bonds (four hydrogen bonds or four covalent Si—O—Si bridges). The main differences between the two systems are that:

(i) *in space*, the squaric acid is a flat (two-dimensional) tecton while the silicic acid is a tetrahedral and then three-dimensional one; and

(ii) *in projection*, the former is tetragonal while the latter is trigonal.

It is reasonable to assume that the crystal chemistry of squarates is a kind of two-dimensional projection of that of silicates with some additional differences due to the tetragonal, instead of trigonal symmetry. This is illustrated in Fig. 11 by representing the C_4O_4 frames by simple squares and the hydroxyl positions by dots. In analogy with silicates, the structural motifs include isolated anions (XX) and (XXIV), single- and double-kinked chains (XVIII), (XXI) and (XXIII), ribbons of double chains (XIX) and tetramers (XXII), while the structure of squaric acid (XVII) is the evident topological transformation of the three-dimensional structure of silica into the plane.

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