Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: OA1013). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Guanidinium Hydrogen Squarate

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Abstract

The unit cell contains two crystallographically independent formula units, $CH_6N_3^+.C_4HO_4^-$, that are connected *via* a three-dimensional network of hydrogen bonds. Two crystallographically independent anion–cation chains are formed and arranged in two crystallographically independent layers and stacked along the *b* axis. The guanidine molecule accepts a proton from the squaric acid. Anions and cations are nearly planar. In the anions, the C—O and especially the C—C bond lengths differ significantly, and the C—C—C angles deviate significantly from 90°.

Comment

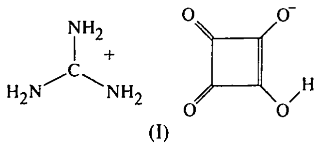
This article is part of a project investigating the non-linear optical properties of new classes of organic compounds involving salts of guanidine derivatives, optically active amines and amino acids with 'oxocarbons' (West, 1980), *i.e.* deltic, squaric, croconic and rhodisonic acids and their sulfur derivatives. The series began with the structure of L-argininium hydrogen squarate (Angelova, Velikova, Kolev & Radomirska, 1996) followed by the structure of *R*-(−)-2-phenylglycinium hydrogen squarate (Angelova, Petrova, Radomirska & Kolev, 1996).

The structures of guanidinium hydrogen oxalate (Adams, 1978) and guanidinium nitrate (Katrusiak & Szafranski, 1994) have been investigated previously. Guanidinium nitrate has phase transitions in the crystal at 296 and 384 K. There is a paucity of structural information for guanidine compounds, even though they have been shown to be cardiovascular, antihistamine and antidiabetic drugs, as well as antibacterial and anti-inflammatory agents (Greenhill & Lue, 1993).

It has been shown that the O atom in guanidinium oxalate monohydrate can accept up to four hydrogen bonds. A search in the chemical literature showed no entry for the title compound. The structures of hydrogen squarates of $[H_2NMe_2]^+$ (Wang & Stucky, 1974), and some alkali (Bull, Ladd, Povey & Shirley, 1973; Semmingsen, 1976) and 3*d* metals such as Co and Ni (Brach, Roziere, Anselment & Peters, 1987) are already known.

The asymmetric unit of the title crystal, (I), contains two guanidinium cations and two hydrogen squarate anions. The anions and cations are nearly planar. The maximum deviations from the best planes defined by the C atom and the N atoms of the cations are 0.09 (4) (H1*B*) and 0.11 (4) Å (H5*A*), and maximum deviations from the best planes defined by the C atoms of the anions are 0.11 (4) (H2) and 0.11 (4) Å (H7). In the anions, the C—C bond lengths at the C atom carrying the OH group [mean values of 1.433 (4) and 1.437 (4) Å] are shorter than the remaining two C—C bond lengths of the ring [mean values of 1.487 (4) and 1.480 (4) Å] and C—C—C angles deviate significantly from 90° [maximum deviation of 3.0 (2)°]. The C—N bond lengths in the cations are in the range 1.318 (4)–1.332 (4) Å, the N—C—N angles in the range 119.3 (3)–121.1 (3)°, the H—N—H angles in the range 114 (4)–129 (4)° and the C—N—H angles in the range 115 (3)–126 (3)°.

A three-dimensional network of hydrogen bonds is observed in the crystal and all H atoms are involved.



(I)

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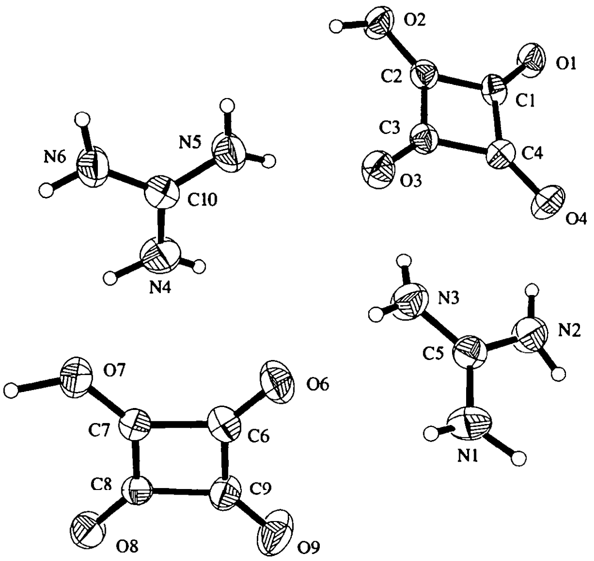

Fig. 1. View of the title compound showing the labelling of all non-H atoms. Displacement ellipsoids are shown at the 50% probability level. H atoms are drawn as circles of arbitrary radii.

The most easily recognisable unit (Fig. 2) is a chain of alternating cations and anions, but there are two such chains: (i) those involving only the ions based on C1–C5, in the region $y = 0$ and parallel to the diagonal (a+c) (further equivalent chains occupy the regions at y = 0.5, 1, *etc.*); (ii) Crystallographically independent, but topologically identical, chains occupy the regions y = 0.25, 0.75, *etc.*; they involve the ions based on C6–C10 and are perpendicular to those of type (i). For clarity, only small sections of the type (ii) chains are shown. Further hydrogen bonds cross-link both independent chain types. Note that the chains do not form hydrogen bonds with their vertically displaced neighbours.

The dihedral angle between the planes through the C atoms of the crystallographically independent hydrogen squarate anions is 68.8 (1)° and the dihedral angle between the planes through the non-H atoms of the two crystallographically independent guanidinium cations is 64.3 (1)°. The corresponding dihedral angles between cation and anion in the two crystallographically independent chains are 6.0 (1) and 14.1 (1)°.

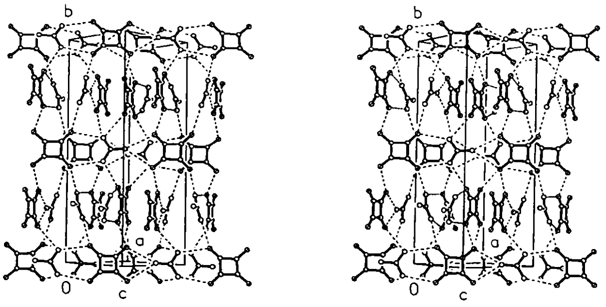

Fig. 2. Stereoscopic view of a section of the crystal structure. Dashed lines indicate contacts with distances shorter than 3.1 Å and D—H···A angles above 130° (possible hydrogen bonds), the geometries of which are given in Table 2.

Experimental

The title compound was prepared by adding an aqueous solution of guanidinium carbonate to a solution of squaric acid in a 1:1 molar ratio. The product was purified by repeated crystallization from doubly distilled water. Colourless crystals were grown by slow evaporation from an aqueous solution at room temperature.

Crystal data

$CH_6N_3^+.C_4HO_4^-$
$M_r = 173.14$
Monoclinic
$P2_1/c$
$a = 8.960 (4)$ Å
$b = 20.536 (11)$ Å
$c = 8.146 (4)$ Å
$\beta = 102.97 (4)°$
$V = 1460.6 (12)$ Å^3
$Z = 8$
$D_x = 1.575$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 7.2–14.4°$
$\mu = 0.137$ mm^{-1}
$T = 291 (2)$ K
Column
1.18 × 0.32 × 0.26 mm
Colourless

Data collection

Siemens $R3m/V$ diffractometer
$\omega–2\theta$ scans
Absorption correction: none
3302 measured reflections
2588 independent reflections
1681 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0285$

$\theta_{\rm max} = 25.05°$
$h = -1 \rightarrow 10$
$k = -24 \rightarrow 1$
$l = -9 \rightarrow 9$
6 standard reflections every 300 reflections frequency: 150 min intensity decay: < 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0562$
$wR(F^2) = 0.1983$
$S = 0.988$
2588 reflections
260 parameters
H-atom coordinates refined
$w = 1/[\sigma^2(F_o^2) + (0.1026P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.288$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.239$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.010 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.268 (3)	C1—C2	1.410 (4)
O2—C2	1.305 (4)	C1—C4	1.478 (4)
O3—C3	1.238 (3)	C2—C3	1.456 (4)
O4—C4	1.233 (3)	C3—C4	1.497 (4)
O6—C6	1.237 (3)	C6—C7	1.444 (4)
O7—C7	1.306 (3)	C6—C9	1.494 (4)
O8—C8	1.271 (3)	C7—C8	1.430 (4)
O9—C9	1.234 (4)	C8—C9	1.466 (4)
O1—C1—C2	132.7 (3)	O6—C6—C7	135.3 (3)
O1—C1—C4	136.9 (3)	O6—C6—C9	136.4 (3)
C2—C1—C4	90.4 (2)	C7—C6—C9	88.3 (2)
O2—C2—C1	130.9 (3)	O7—C7—C8	136.3 (3)

O2—C2—C3	136.1 (3)	O7—C7—C6	131.2 (3)
C1—C2—C3	93.0 (2)	C8—C7—C6	92.5 (2)
O3—C3—C2	136.9 (3)	O8—C8—C7	138.1 (3)
O3—C3—C4	135.2 (3)	O8—C8—C9	131.9 (3)
C2—C3—C4	87.9 (2)	C7—C8—C9	90.0 (2)
O4—C4—C1	136.8 (3)	O9—C9—C8	133.1 (3)
O4—C4—C3	134.5 (3)	O9—C9—C6	137.8 (3)
C1—C4—C3	88.7 (2)	C8—C9—C6	89.1 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O8^{i}	1.04 (3)	1.46 (3)	2.488 (3)	167 (3)
O7—H7···O1	1.06 (3)	1.41 (3)	2.462 (3)	174 (3)
N1—H1*A*···O2^{ii}	0.86 (3)	2.29 (3)	2.934 (4)	132 (3)
N1—H1*B*···O1^{ii}	0.89 (3)	2.29 (3)	3.009 (4)	138 (3)
N3—H3*B*···O6^{iii}	0.85 (3)	2.06 (3)	2.903 (4)	170 (3)
N3—H3*A*···O3^{iv}	0.87 (3)	2.02 (3)	2.873 (4)	168 (3)
N2—H2*A*···O4^{iv}	0.89 (3)	2.08 (3)	2.960 (4)	170 (3)
N2—H2*B*···O9^{v}	0.86 (3)	2.01 (3)	2.871 (4)	172 (3)
N5—H5*B*···O9^{v}	0.86 (4)	2.19 (4)	2.994 (5)	154 (3)
N6—H6*B*···O8^{v}	0.89 (4)	1.99 (3)	2.865 (4)	169 (3)
N6—H6*A*···O4^{vi}	0.88 (3)	2.09 (4)	2.929 (4)	160 (3)
N4—H4*B*···O7^{vii}	0.88 (4)	2.14 (4)	2.927 (4)	148 (3)
N4—H4*A*···O6^{vii}	0.90 (3)	2.23 (4)	2.997 (4)	142 (3)
N5—H5*A*···O3^{viii}	0.91 (3)	2.06 (3)	2.959 (4)	170 (3)

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

The title complex was characterized by elemental analysis and spectroscopic methods. The solid-state IR spectrum (KBr pellets) confirms that only one hydroxyl group is 'free' and that the guanidine molecule is protonated. The strong peaks at 3475 and 3184 cm^{-1}, and the other bands around 3000 cm^{-1} show the existence of a network of strong hydrogen bonds. The melting point of guanidinium hydrogen squarate is over 580 K with decomposition. The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1990) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (*SHELXL*93; Sheldrick, 1993). All H atoms were taken from difference Fourier maps and refined with restrained O—H and N—H distances (*SADI* 0.03), and U_{iso} constrained to be $1.5U_{eq}$ of the carrier atom. The crystal was slightly longer than the beam diameter, which may lead to small systematic errors in *U* values.

Data collection: *R*3*m*/*V* software. Cell refinement: *R*3*m*/*V* software. Data reduction: *R*3*m*/*V* software. Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL*93 and *PARST*95 (Nardelli, 1995).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: JZ1154). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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α-Formylphenylacetonitrile in the Solid State at 220 K

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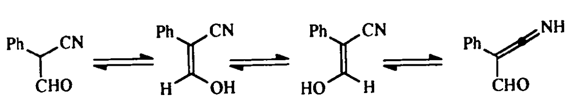
Abstract

The title compound, 3-hydroxy-2-phenylpropenonitrile (α-hydroxymethylene-α-phenylacetonitrile), C_9H_7NO, exists in the solid state as the *Z*-enol tautomer, forming one-dimensional chains *via* hydrogen bonding between the enol OH group and the nitrile N atom.

Comment

The title compound, (1), which is a useful intermediate in heterocyclic synthesis, can, in principle, exist in three tautomeric forms (see scheme below), one of which can occur as *Z* and *E* isomers [(1*b*) and (1*b*′), respectively]. In solution, (1) is present as a 1:1 mixture of (1*b*) and (1*b*′) (Kirsch, Mieloszynski, Paquer & Andrieu, 1983), and the present study was undertaken in order to establish whether this persists in the solid state.



(1*a*) (1*b*) (1*b*′) (1*c*)

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