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Anhydrous guanidinium hydrogen fumarate: a two-dimensional hydrogen-bonded network structure

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Key indicators

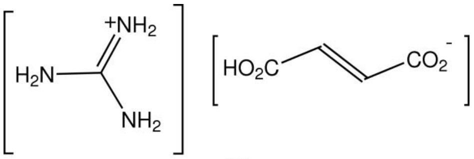
Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.002 Å
R factor = 0.040
wR factor = 0.143
Data-to-parameter ratio = 12.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $CH_6N_3^+\cdot C_4H_3O_4^-$, forms a two-dimensional hydrogen-bonded network structure. The guanidinium cations lie across crystallographic mirror planes while the hydrogen fumarate anions have inversion symmetry with the acid proton 50% disordered over the two carboxylate groups.

Comment

The known structures of guanidinium salts with diprotic aliphatic acids are not common and many are acid salts (Adams, 1978; Andrews *et al.*, 1979; Leban & Rupnik, 1992; Zyss *et al.*, 1993; Krumbe *et al.*, 1989; Krumbe & Haussuehl, 1987; Golic *et al.*, 1985; Froehlich *et al.*, 1985).



(I)

Since the incorporation of water molecules of hydration in guanidinium salts is dependent on the choice of solvent, we carried out the synthesis of (I) in 50% propan-2-ol–water to obtain the anhydrous 1:1 salt reported here. The centrosymmetric $P2_1/m$ model (rather than the $P2_1$ model which was tried but gave poor refinement and low precision) places the guanidinium cation across a crystallographic mirror plane and the hydrogen fumarate anion across an inversion centre. This requires the single acid proton to be 50% disordered over the

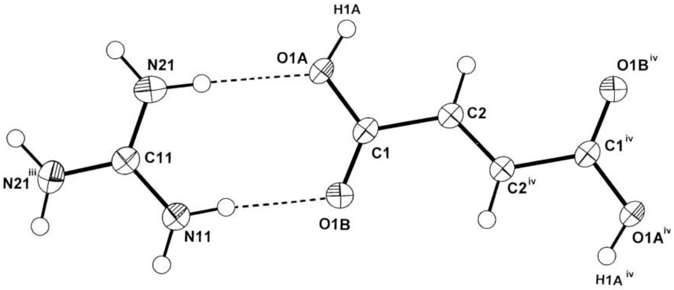


Figure 1
Molecular structure and atom-naming scheme for the guanidinium cation and the hydrogen fumarate anion in (I). Displacement ellipsoids are drawn at the 50% probability level. The guanidinium atoms N21 and N21^{iii} are related by mirror symmetry while the fumarate atoms designated (iv) are inversion-related [symmetry codes: (iii) $x, -y+\frac{1}{2}, z$; (iv) $-x, -y, -z+1$]. The fumarate acid protons H1*A* and H1*A*^{iv} are 50% disordered over the two carboxylate groups. Dashed lines indicate hydrogen bonds.

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two *trans*-related carboxylate groups (Fig. 1). All available proton donors and acceptors are involved in hydrogen-bonding interactions (Table 1), giving a two-dimensional layered network structure (Fig. 2). For the guanidinium cation, there are six cyclic associations [two $R_2^2(8)$, two $R_4^2(10)$ and two $R_3^2(11)$]. The two mirror-related 11-membered rings are closed by single *anti*-related fumaric acid H atoms which also give intermolecular *anti*-associations with fumarate-O acceptors in strong O1*A*···O1*A*$^{\text{i}}$ hydrogen bonds (Table 1).

Experimental

The title compound was synthesized by heating together fumaric acid (1 mmol) and guanidinium carbonate (0.5 mmol) in 50 ml of 50% propan-2-ol–water under reflux for 10 min. After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solution gave colourless crystal plates (m.p. 495–497 K).

Crystal data

$CH_6N_3^+ \cdot C_4H_3O_4^-$
$M_r = 175.15$
Monoclinic, $P2_1/m$
$a = 5.4995$ (12) Å
$b = 18.842$ (5) Å
$c = 3.6943$ (11) Å
$\beta = 94.83$ (2)°
$V = 381.45$ (17) Å^3

$Z = 2$
$D_x = 1.525$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.13$ mm^{-1}
$T = 297$ (2) K
Plate, colourless
0.45 × 0.32 × 0.12 mm

Data collection

Rigaku AFC-7R diffractometer
ω–2θ scans
Absorption correction: none
1088 measured reflections
905 independent reflections
637 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$
$\theta_{\max} = 27.5°$
3 standard reflections
frequency: 150 min
intensity decay: 2.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.143$
$S = 0.94$
905 reflections
74 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.0662P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···O1*A*$^{\text{i}}$	0.85 (4)	1.63 (4)	2.4658 (18)	166 (5)
N11—H11···O1*B*	0.88 (3)	1.99 (3)	2.873 (2)	174 (2)
N21—H21*A*···O1*B*$^{\text{ii}}$	0.92 (3)	2.19 (3)	3.006 (2)	148 (3)
N21—H21*B*···O1*A*	0.89 (3)	2.10 (3)	2.991 (2)	175 (3)

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

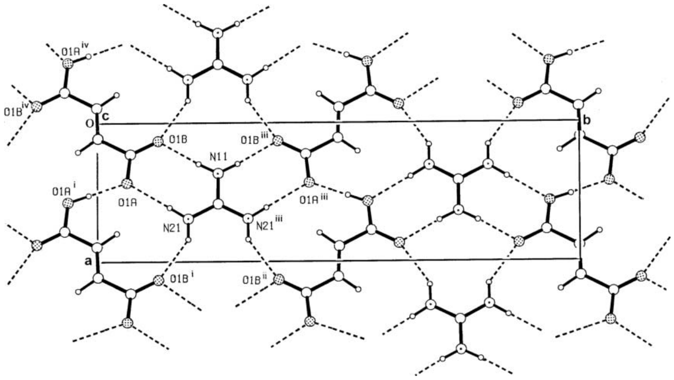

Figure 2
The hydrogen-bonded sheet structure of (I) viewed down the *c* axial direction, showing hydrogen-bonding associations as dashed lines. For symmetry codes, see Fig. 1 caption and Table 1.

The guanidinium H atoms and the fumarate acid H atom were located by difference methods and their positional and isotropic displacement parameters were refined. The fumarate ethylenic H atom was included in the refinement in a calculated position (C—H = 0.94 Å) using a riding-model approximation, with $U_{\text{iso}}(\text{H}) = U_{\text{eq}}(\text{C})$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* for Windows (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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