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# Guanidinium 2-amino-4-nitrobenzoate monohydrate at 130 K

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**Key indicators**

Single-crystal X-ray study
$T$ = 130 K
Mean $\sigma$(C–C) = 0.002 Å
$R$ factor = 0.040
$wR$ factor = 0.108
Data-to-parameter ratio = 9.7

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

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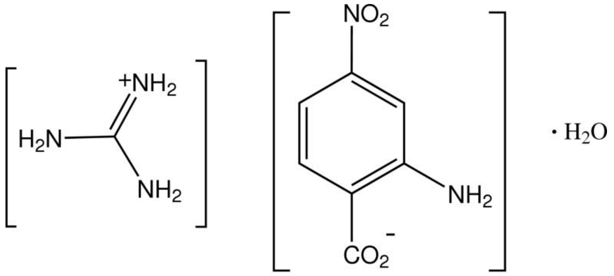
Guanidinium 4-nitroanthranilate monohydrate, $CH_6N_3^+\cdot C_7H_5N_2O_4^-\cdot H_2O$, determined at 130 K, forms a primary hydrogen-bonded ribbon structure through cyclic hydrogen-bonding interactions involving all six protons of the guanidinium cation with the amino N-atom and carboxylate O-atom acceptors of the anion, and the water molecule of solvation. Other interactions, including the water molecule bridging the primary ribbons, give a three-dimensional structure.

## Comment

Although guanidine (GU) may be readily protonated by most organic acids, the crystal structures of guanidinium carboxylates are not common. Among examples of these, all of those with aliphatic acids involve diprotic acids: oxalic acid (a 1:1 monohydrate) (Adams, 1978; Andrews *et al.*, 1979), acetylenedicarboxylic acid (a 1:1 anhydrate) (Leban & Rupnik, 1992), tartaric acid [a 1:1 anhydrate (Zyss *et al.*, 1993) and a 2:1 monohydrate (Krumbe *et al.*, 1989)] and aspartic acid (a 1:1 anhydrate) (Krumbe & Haussühl, 1987). The aromatic examples, which are all anhydrous except for the compound with pyrazine-2,3-dicarboxylic acid (a 2:1 trihydrate) (Smith *et al.*, 2006), are with 4-amino-3,5,6-trichloropicolinic acid (1:1) (Parthasarathi *et al.*, 1982), 3,5-dinitrosalicylic acid (1:1) (Smith *et al.*, 2001), 4-hydroxypyridine-2,6-dicarboxylic acid (1:1) (Moghimi *et al.*, 2005) and pyromellitic acid (2:1) (Sun *et al.*, 2002).



(I)

We have used 2-amino-4-nitrobenzoic acid (4-nitroanthranilic acid, NAA) for cocrystal formation with Lewis bases, but its efficacy in such processes is poor. Crystallographically characterized examples are the proton-transfer compounds with ethylenediamine (a 1:2 dihydrate) (Smith *et al.*, 2002) and dicyclohexylamine (a 1:1 anhydrate) (Smith *et al.*, 2004). Crystals of the title compound, guanidinium 4-nitroanthranilate monohydrate, (I), were obtained from the 1:1 stoichiometric reaction of NAA with guanidine carbonate and the crystal structure is reported here. An initial room-

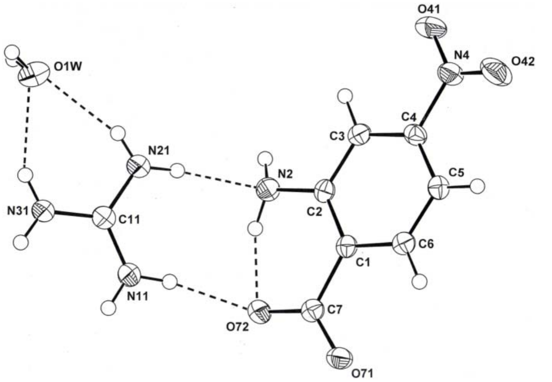


**Figure 1**
The molecular configuration, atom-naming scheme and inter-species hydrogen bonding (shown as dashed lines) for the GU cation, the NAA anion and the water molecule of solvation in (I). Displacement ellipsoids are drawn at the 50% probability level.

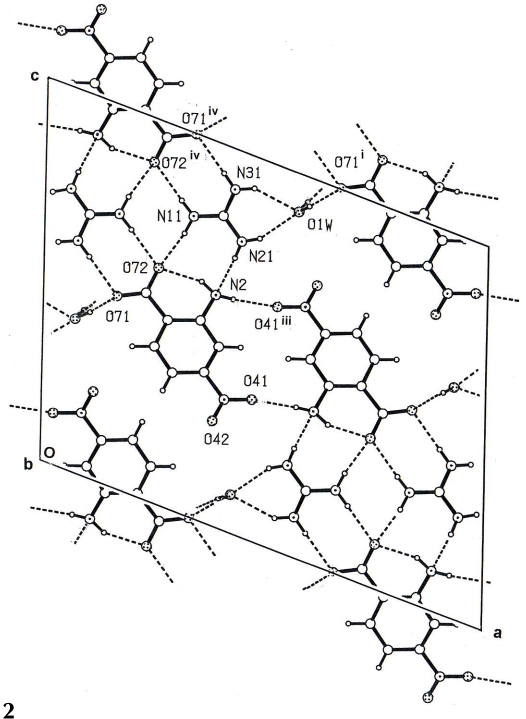


**Figure 2**
The packing in the unit cell, viewed down the *b*-axis direction, showing hydrogen-bonding associations (dashed lines). For symmetry codes, see Table 1.

temperature structure gave poor intensity data and significant disorder in the NAA nitro group necessitating this low-temperature redetermination in which both problems were resolved.

In (I) (Fig. 1), all six protons of the GU cation, together with those of the amino substituent group of the NAA anion and the water molecule of hydration make hydrogen-bonding interactions with carboxylate and nitro O-atom acceptors (Table 1), resulting in a three-dimensional layered structure (Fig. 2). With the GU cation, three types of symmetric cyclic interactions are present: an $R_2^2(10)$ interaction with an amine N and a carboxylate O atom, an $R_2^1(6)$ interaction with the water molecule and an $R_2^2(8)$ interaction with the NAA carboxylate group. One of the amine H atoms forms an intramolecular hydrogen bond with a carboxylate O atom, while the second gives structure extension along the *a*-axis direction *via* a weak centrosymmetric N—H···O(nitro) link. The water molecule also provides a symmetrical three-dimensional hydrogen-bonding link between the sheets through carboxylate atom O7.

In the NAA anions, both the carboxylate and nitro groups are essentially coplanar with the benzene ring [C2—C1—C7—O71 = 173.25 (14)° and C3—C4—N4—O42 = 173.60 (15)°].

## Experimental

The title compound was synthesized by heating together 1 mmol quantities of 2-amino-4-nitrobenzoic acid (4-nitroanthranilic acid, NAA) and guanidine carbonate ($GU_2CO_3$) in 50% isopropyl alcohol–water (50 ml) under reflux for 10 min. After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solution gave orange prisms (m.p. 524–525 K).

*Crystal data*

$CH_6N_3^+ \cdot C_7H_5N_2O_4^- \cdot H_2O$
$M_r = 259.23$
Monoclinic, $P2_1/n$
$a = 16.122$ (5) Å
$b = 3.7796$ (11) Å
$c = 19.715$ (5) Å
$\beta = 110.006$ (5)°
$V = 1128.8$ (6) Å$^3$
$Z = 4$
$D_x = 1.525$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 0.13$ mm$^{-1}$
$T = 130$ (2) K
Plate, yellow
0.45 × 0.40 × 0.10 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.92$, $T_{max} = 0.98$
5221 measured reflections
1966 independent reflections
1677 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 25.0°$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.108$
$S = 1.02$
1966 reflections
203 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.066P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å$^{-3}$
$\Delta\rho_{min} = -0.21$ e Å$^{-3}$

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1*W*—H11*W*···O71$^{i}$ | 0.88 (3) | 1.90 (3) | 2.755 (2) | 162 (2) |
| O1*W*—H12*W*···O71$^{ii}$ | 0.91 (3) | 1.83 (3) | 2.738 (2) | 175 (2) |
| N2—H2*A*···O41$^{iii}$ | 0.858 (19) | 2.246 (19) | 3.101 (2) | 174.2 (17) |
| N2—H2*B*···O72 | 0.89 (2) | 1.93 (2) | 2.632 (2) | 133.9 (17) |
| N11—H11···O72 | 0.87 (2) | 2.07 (2) | 2.935 (2) | 170.1 (18) |
| N11—H12···O72$^{iv}$ | 0.84 (2) | 2.01 (2) | 2.848 (2) | 173.5 (18) |
| N21—H21···N2 | 0.88 (2) | 2.17 (2) | 3.049 (2) | 174 (2) |
| N21—H22···O1*W* | 0.810 (18) | 2.156 (18) | 2.914 (2) | 155.7 (18) |
| N31—H31···O1*W* | 0.84 (2) | 2.11 (2) | 2.863 (2) | 148.1 (19) |
| N31—H32···O71$^{iv}$ | 0.84 (2) | 2.02 (2) | 2.854 (2) | 173.9 (15) |

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

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H atoms involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic displacement parameters were refined. The aromatic H atoms were included in the refinement in calculated positions (C—H = 0.95 Å) using a riding-model approximation, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); 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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