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Anhydrous guanidinium 3,5-dinitrobenzoate

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Guanidinium 3,5-dinitrobenzoate, $CH_6N_3^+ \cdot C_7H_3N_2O_6^-$, determined at 130 K, forms a three-dimensional hydrogen-bonded structure involving all six H atoms of the guanidinium cation with oxygen acceptors of the anion including an offset cyclic $R_2^2(8)$ interaction with the carboxylate group.

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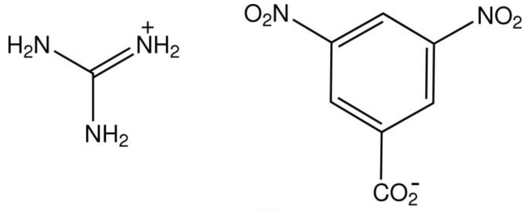
Comment

Guanidine (GU) reacts with most carboxylic acids but the number of crystallographically characterized examples of these salts is not large. With aromatic and heteroaromatic acids, most compounds are anhydrous, *e.g.* guanidinium 4-amino-3,5,6-trichloropicolinate (Parthasarathi *et al.*, 1982), guanidinium 3,5-dinitrosalicylate (Smith *et al.*, 2001), guanidinium 4-hydroxypyridinium-2,6-dicarboxylate (Moghimi *et al.*, 2005) and bis(guanidinium) pyromellitate (Sun *et al.*, 2002). Hydrate examples are the compounds with pyrazine-2,3-dicarboxylic acid (a 2:1 trihydrate) (Smith *et al.*, 2006) and 4-nitroanthranilic acid (a 1:1 monohydrate) (Smith *et al.*, 2007).



(I)

Although 3,5-dinitrobenzoic acid (3,5-DNBA) has been used for the synthesis of crystalline designer compounds (Etter & Frankenbach, 1989), the structure of the guanidiniun salt has not previously been reported. We obtained large crystals of the title compound, anhydrous guanidinium 3,5-dinitrobenzoate, $[CH_6N_3]^+$ $[C_7H_3N_3O_6]^-$, (I), from the 1:1 stoichiometric reaction of 3,5-DNBA with guanidine carbonate in 50% propan-2-ol–water and the crystal structure is reported here.

In (I) (Fig. 1), all six H atoms of the GU cation give hydrogen-bonding interactions with carboxylate and, to a lesser extent, nitro O acceptors of the anion (Table 1), resulting in a three-dimensional framework structure (Fig. 2). Among these is a cyclic $R_2^2(8)$ interaction with the two carboxylate oxygen acceptors of the anion, similar to that found in the analogous guanidinium 3,5-dinitrosalicylate, except that the two interacting species are offset rather than coplanar. In (I) both carboxylate O atoms also act as acceptors in secondary hydrogen-bonding interactions.

Key indicators

Single-crystal X-ray study
T = 130 K
Mean σ(C–C) = 0.002 Å
R factor = 0.030
wR factor = 0.082
Data-to-parameter ratio = 9.8

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

In the 3,5-DNBA anions both the carboxylate and the nitro groups are rotated slightly out of the plane of the benzene ring [torsion angles: C2—C1—C7—O71 = 165.45 (12)°, C2—C3—N3—O32 = −174.96 (11)° and C4—C5—N5—O52 = 166.42 (11)°].

Experimental

The title compound was synthesized by heating together 1 mmol quantities of 3,5-dinitrobenzoic acid (3,5-DNBA) and guanidinium carbonate in 50 ml of 50% propan-2-ol–water under reflux for 10 minutes. After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solution gave pale-yellow crystal blocks (m.p. > 553 K).

Crystal data

$CH_6N_3^+\cdot C_7H_3N_2O_6^-$
$M_r = 271.20$
Monoclinic, $P2_1/n$
$a = 7.5192\ (6)$ Å
$b = 19.0605\ (14)$ Å
$c = 7.8416\ (6)$ Å
$\beta = 103.566\ (1)°$
$V = 1092.50\ (15)$ Å^3

$Z = 4$
$D_x = 1.649$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.14$ mm^{-1}
$T = 130\ (2)$ K
Block, pale yellow
$0.35 \times 0.30 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
5679 measured reflections

1920 independent reflections
1753 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\rm max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.082$
$S = 1.03$
1920 reflections
196 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.2176P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.23$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11A···O71$^{\rm i}$	0.853 (16)	2.035 (15)	2.8376 (16)	156.6 (14)
N11—H11B···O72$^{\rm ii}$	0.889 (16)	1.919 (15)	2.7933 (17)	167.4 (15)
N21—H21A···O51$^{\rm iii}$	0.857 (15)	2.549 (15)	3.1979 (15)	133.3 (11)
N21—H21B···O71	0.887 (17)	1.966 (17)	2.8499 (15)	174.2 (15)
N31—H31A···O72	0.837 (15)	2.182 (15)	3.0017 (16)	166.5 (14)
N31—H31B···O32$^{\rm iv}$	0.830 (16)	2.590 (16)	3.1371 (16)	124.7 (13)
N31—H31B···O71$^{\rm i}$	0.830 (16)	2.422 (16)	3.0954 (16)	138.9 (13)

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

H atoms involved in hydrogen-bonding interactions were located by difference Fourier 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 $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

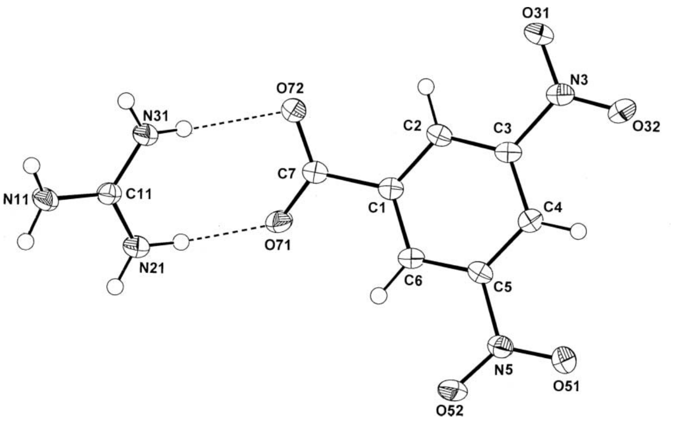


Figure 1
The structure, atom-naming scheme and inter-species hydrogen bonding (shown as dashed lines) for the GU cation and the DNBA anion in (I). Displacement ellipsoids are drawn at the 50% probability level.

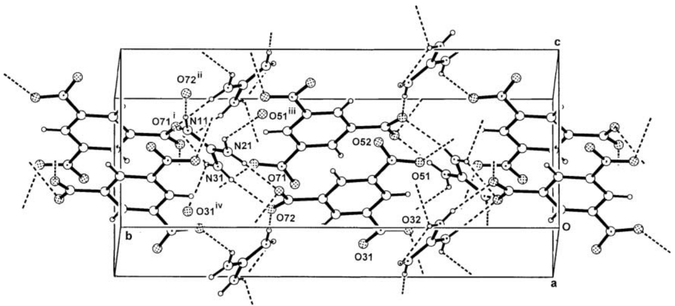


Figure 2
Perspective view of the packing of (1) in the unit cell viewed approximately down the approximate *a* axial direction, showing hydrogen-bonding associations. For symmetry codes, see Table 1.

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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References

Bruker (1999). *SAINT*. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2000). *SMART*. Version 5.55. Bruker AXS Inc., Madison, Wisconsin, USA.
Etter, M. C. & Frankenbach, G. M. (1989). *Chem. Mater.* **1**, 10–12.
Moghimi, A., Aghabozorg, H., Soleimannejad, J. & Ramezanipour, F. (2005). *Acta Cryst.* E**61**, o442–o444.
Parthasarathi, V., Wolfrum, S., Noordik, J. H., Beurskins, P. T., Smith, G., O'Reilly, E. J. & Kennard, C. H. L. (1982). *Cryst. Struct. Commun.* **11**, 1519–1524.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*, University of Göttingen, Germany.
Smith, G., Bott, R. C. & Wermuth, U. D. (2001). *Acta Cryst.* E**57**, o640–o642.
Smith, G., Wermuth, U. D., Healy, P. C. & White, J. M. (2007). *Acta Cryst.* E**63**, o7–o9.
Smith, G., Wermuth, U. D., Young, D. J. & White, J. M. (2006). *Acta Cryst.* E**62**, o3912–o3914.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Sun, Y.-Q., Zhang, J. & Yang, G.-Y. (2002). *Acta Cryst.* E**58**, o904–o906.

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