Anhydrous guanidinium 3,5-dinitrobenzoate

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Key indicators

Single-crystal X-ray study

 $T = 130\text{ K}$ Mean $\sigma(\text{C}—\text{C}) = 0.002\text{ \AA}$ 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>.

Guanidinium 3,5-dinitrobenzoate, $\text{CH}_6\text{N}_3^+ \cdot \text{C}_7\text{H}_3\text{N}_2\text{O}_6^-$, 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).

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 guanidinium salt has not previously been reported. We obtained large crystals of the title compound, anhydrous guanidinium 3,5-dinitrobenzoate, $[\text{CH}_6\text{N}_3]^+ [\text{C}_7\text{H}_3\text{N}_2\text{O}_6]^-$, (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.

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

CH₆N₃⁺·C₇H₃N₂O₆[−]
M_r = 271.20
 Monoclinic, *P*2₁/*n*
a = 7.5192 (6) Å
b = 19.0605 (14) Å
c = 7.8416 (6) Å
 β = 103.566 (1)°
V = 1092.50 (15) Å³

Z = 4
D_x = 1.649 Mg m^{−3}
 Mo *K*α radiation
 μ = 0.14 mm^{−1}
T = 130 (2) K
 Block, pale yellow
 0.35 × 0.30 × 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* > 2σ(*I*)
*R*_{int} = 0.042
 $\theta_{\max}$ = 25.0°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.20 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e \AA}^{-3}$

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N11—H11A...O71 ⁱ	0.853 (16)	2.035 (15)	2.8376 (16)	156.6 (14)
N11—H11B...O72 ⁱⁱ	0.889 (16)	1.919 (15)	2.7933 (17)	167.4 (15)
N21—H21A...O51 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 ^{iv}	0.830 (16)	2.590 (16)	3.1371 (16)	124.7 (13)
N31—H31B...O71 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*_{iso}(H) = 1.2*U*_{eq}(C).

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

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.

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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