organic compounds

Guanidinium 4-aminobenzoate

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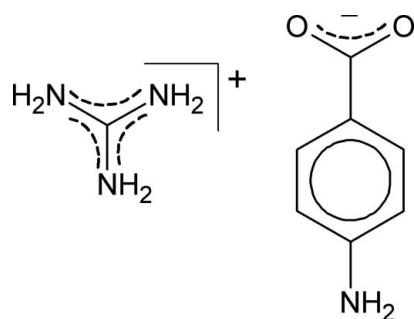Correspondence e-mail: psidonio@pollux.fis.uc.pt

In the title compound, $CH_6N_3^+ \cdot C_7H_6NO_2^-$, the cation and anion lie on crystallographic mirror planes. The 4-amino-benzoate anion is almost in a planar conformation with a maximum deviation of 0.024 (2) Å for the N atom. The bond length in the deprotonated carboxyl group is intermediate between those of normal single and double Csp^2=O bonds, indicating delocalization of the charge over both O atoms of the COO^- group. In the crystal, N—H···O hydrogen bonds assemble the ions in layers propagating in the bc plane. This structure is very similar to that of guanidinium benzoate.

Related literature

For a related structure, see: Pereira Silva et al. (2007). 4-Aminobenzoic acid has two known polymorphs, see: Gracin & Rasmuson (2004). For the potential applications of guanidine compounds in non-linear optics, see: Zyss et al. (1993). For bond-length data, see: Allen et al. (1987).

Experimental

Crystal data

$CH_6N_3^+ \cdot C_7H_6NO_2^-$	V = 1023.36 (4) Å^3
M_r = 196.22	Z = 4
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
a = 14.9833 (4) Å	μ = 0.10 mm^{-1}
b = 8.0602 (2) Å	T = 293 K
c = 8.4737 (2) Å	$0.33 \times 0.19 \times 0.15$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer	19879 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	1323 independent reflections
T_{min} = 0.898, T_{max} = 0.986	960 reflections with $I > 2\sigma(I)$
	R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.109	
S = 1.04	
1323 reflections	$\Delta\rho_{max}$ = 0.13 e Å^{-3}
85 parameters	$\Delta\rho_{min}$ = -0.20 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1^i	0.940 (15)	1.869 (16)	2.8068 (14)	175.4 (13)
N1—H1B···O1^{ii}	0.875 (16)	2.107 (16)	2.9032 (15)	151.0 (13)
N2—H2A···O1^{ii}	0.923 (16)	2.099 (16)	2.9408 (8)	151.1 (12)

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

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

References

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supporting information

Guanidinium 4-aminobenzoate

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S1. Comment

Guanidine is a strong Lewis base and the guanidinium cation may be easily anchored onto numerous inorganic and organic anions and polyanions, largely because of the presence of six potential donor sites for hydrogen-bonding interactions. From the point of view of their physical properties, guanidine compounds are potentially interesting for non-linear optics applications since guanidinium, a polarizable acentric two-dimensional cation, can be regarded as a planar octupolar chemical entity (Zyss *et al.*, 1993). We are currently engaged in a research project aimed at investigating the structures, and the dielectric and optical properties of guanidine and guanidine derivative compounds.

   4-Aminobenzoic acid has two known polymorphs (Gracin & Rasmuson, 2004) and is one of the most versatile acids for structure extension by linear hydrogen-bonding associations, through both the carboxylic acid and the amine functional groups.

   Both ions of the title compound, (I), Fig. 1, possess mirror symmetry, with the C6 and N2 atoms of the cation situated in the mirror plane as well as the carboxylate group C atom, the ipso-C and the para-C and N atoms of the anion.

   The 4-aminobenzoate anion is almost in a planar conformation, with the atoms N4 and C5 displaced from the ring plane by about the same amounts, 0.024 (2) and 0.022 (2)Å respectively, and in the same direction.

   The dihedral angle between the phenyl ring and the carboxylate group [1.58 (16)°] is slightly larger than the corresponding angle in guanidinium benzoate [0.41 (18)°].

   The O—C—O angle of the carboxylate group is greater than 120° because of the steric effect of lone-pair electrons on both O atoms. The bond length in the deprotonated carboxyl group is intermediate between the single Csp^2—O (1.308-1.320 Å) and double Csp^2=O bond lengths (1.214-1.224 Å, Allen *et al.*, 1987), indicating delocalization of the charge over both O atoms of the COO^- group.

   The three C—N bond lengths in the propeller-shaped $(CH_6N_3)^+$ cation are similar (Table 1), the symmetry of the cation being C_{3h}. The usual model of electron delocalization in this species, leading to a C—N bond order of 1.33, is applicable here.

   All H atoms on the guanidinium cation are involved in N—H···O interactions with the anion (Fig. 2, Table 2) forming infinite layers propagating in the bc plane, each carboxylate O atom accepting three hydrogens. In each layer the cation is bonded to three anions, two approximately perpendicular and one approximately coplanar (Fig. 3). This pattern is also found in guanidinium benzoate (Pereira Silva *et al.*, 2007).

S2. Experimental

The title compound was prepared by adding 4-aminobenzoic acid (Aldrich, 99%, 1.0 mmol) to guanidinium carbonate (Aldrich 99%, 0.5 mmol) in a water solution (100 ml). The solution was slowly warmed to the boiling point and then left to evaporate under ambient conditions. After 2 weeks, small light brown single crystals were obtained.

S3. Refinement

All H atoms were located in a difference Fourier synthesis. The guanidinium H-atom coordinates were refined, with $U_{iso}(H) = 1.2U_{eq}(N)$. The H atoms of the anion were placed in calculated positions and refined as riding on their parent atoms, using SHELXL97 (Sheldrick, 2008) defaults [C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$].
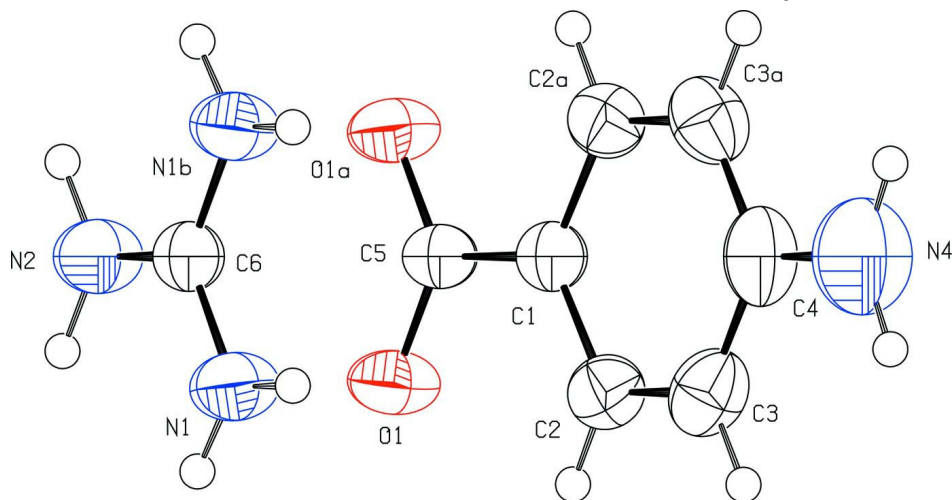
Figure 1

A plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (a);(b) x, 1/2-y, z]
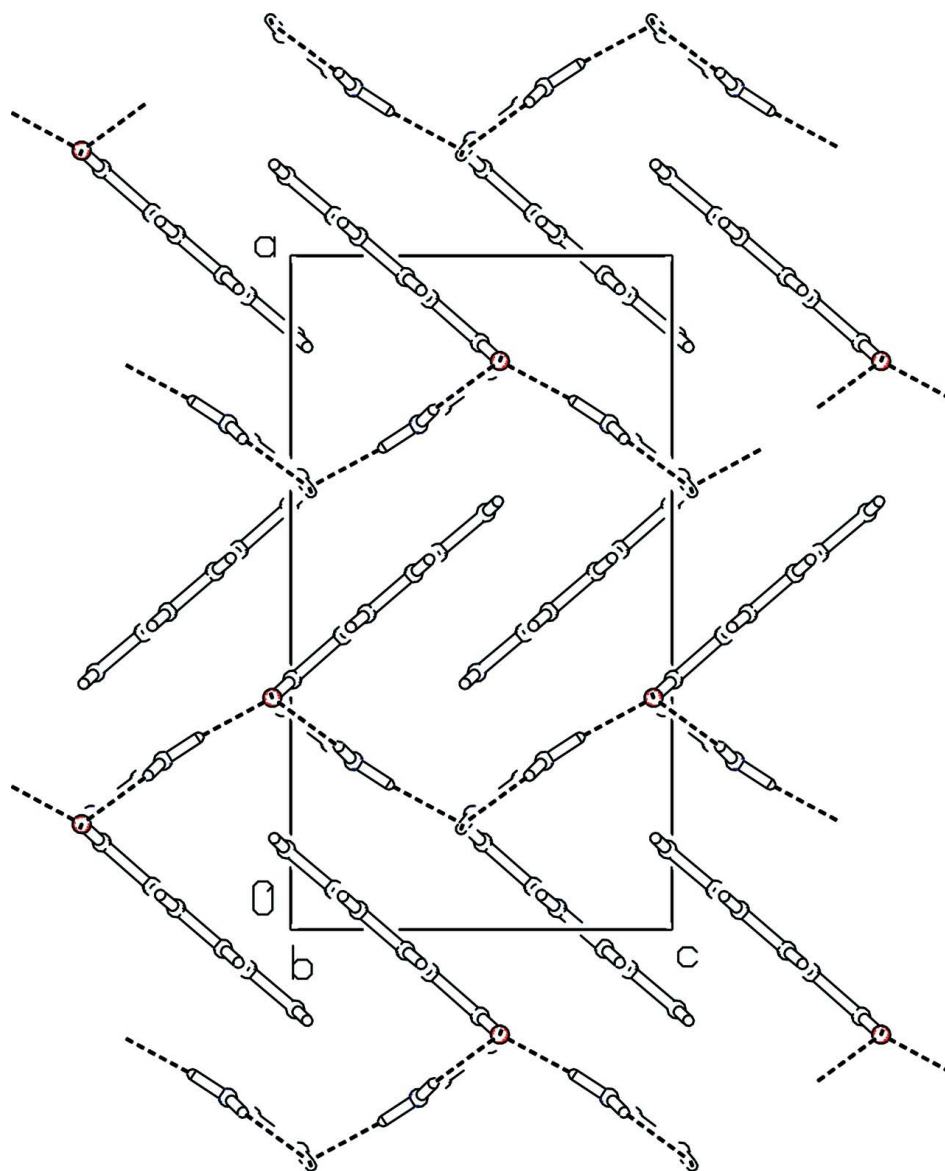
Figure 2

A packing diagram for (I), viewed down the b axis, showing the layer formation. Hydrogen bonds are shown as dashed lines.
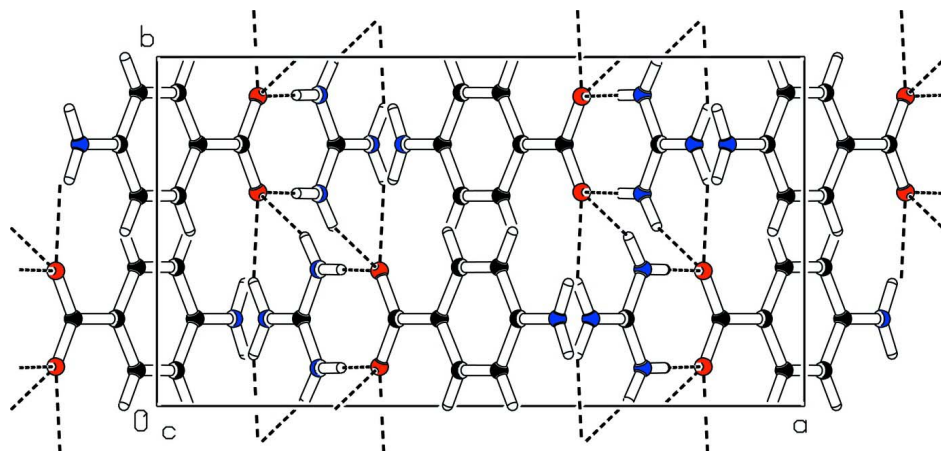
Figure 3

A packing diagram for (I), viewed down the c axis, with the hydrogen bonds depicted by dashed lines.

Guanidinium 4-aminobenzoate

Crystal data

CH$_6$N$_3$$^+$·C$_7H_6NO_2$$^-$

$M_r = 196.22$

Orthorhombic, *Pnma*

Hall symbol: -P 2ac 2n

$a = 14.9833$ (4) Å

$b = 8.0602$ (2) Å

$c = 8.4737$ (2) Å

$V = 1023.36$ (4) Å^3

$Z = 4$

$F(000) = 416$

$D_x = 1.274$ Mg m^{-3}

Mo *Kα* radiation, $\lambda = 0.71073$ Å

Cell parameters from 8009 reflections

$\theta = 2.8$–27.5°

$\mu = 0.10$ mm^{-1}

$T = 293$ K

Irregular edge, light brown

$0.33 \times 0.19 \times 0.15$ mm

Data collection

Bruker APEX2 CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)

$T_{min} = 0.898$, $T_{max} = 0.986$

19879 measured reflections

1323 independent reflections

960 reflections with $I > 2\sigma(I)$

$R_{int} = 0.026$

$\theta_{max} = 28.1°$, $\theta_{min} = 2.7°$

$h = -18 \rightarrow 19$

$k = -10 \rightarrow 9$

$l = -10 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.109$

$S = 1.04$

1323 reflections

85 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.051P)^2 + 0.1635P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.13$ e Å^{-3}

$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
O1	0.34385 (6)	0.11290 (10)	−0.04842 (10)	0.0519 (3)
C1	0.43652 (10)	0.2500	0.13590 (17)	0.0390 (4)
C2	0.46854 (8)	0.10235 (14)	0.19926 (13)	0.0462 (3)
H2	0.4490	0.0019	0.1577	0.055*
C3	0.52869 (8)	0.10183 (16)	0.32253 (14)	0.0542 (3)
H3	0.5491	0.0015	0.3630	0.065*
C4	0.55904 (11)	0.2500	0.3867 (2)	0.0556 (5)
C5	0.37086 (10)	0.2500	0.00390 (17)	0.0391 (4)
N4	0.61881 (15)	0.2500	0.5120 (3)	0.0886 (7)
H4	0.6353 (13)	0.149 (3)	0.543 (2)	0.106*
N1	0.25025 (7)	0.10833 (13)	0.66469 (14)	0.0551 (3)
H1A	0.2845 (9)	0.1093 (16)	0.7576 (18)	0.066*
H1B	0.2285 (9)	0.016 (2)	0.6258 (17)	0.066*
N2	0.17018 (11)	0.2500	0.47745 (19)	0.0563 (4)
H2A	0.1493 (9)	0.147 (2)	0.4470 (16)	0.068*
C6	0.22330 (11)	0.2500	0.6031 (2)	0.0426 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0705 (6)	0.0334 (4)	0.0519 (5)	−0.0031 (4)	−0.0139 (4)	−0.0006 (3)
C1	0.0415 (8)	0.0398 (8)	0.0358 (7)	0.000	0.0050 (6)	0.000
C2	0.0489 (6)	0.0455 (6)	0.0442 (6)	0.0021 (5)	0.0014 (5)	0.0013 (5)
C3	0.0530 (7)	0.0627 (8)	0.0467 (7)	0.0100 (6)	−0.0004 (5)	0.0089 (6)
C4	0.0443 (9)	0.0813 (14)	0.0411 (9)	0.000	−0.0018 (8)	0.000
C5	0.0460 (8)	0.0335 (8)	0.0380 (8)	0.000	0.0035 (7)	0.000
N4	0.0818 (13)	0.1110 (19)	0.0732 (13)	0.000	−0.0344 (11)	0.000
N1	0.0655 (7)	0.0379 (6)	0.0618 (7)	0.0026 (5)	−0.0206 (5)	−0.0012 (5)
N2	0.0656 (10)	0.0446 (9)	0.0587 (9)	0.000	−0.0226 (8)	0.000
C6	0.0419 (8)	0.0398 (8)	0.0460 (8)	0.000	−0.0036 (7)	0.000

Geometric parameters (Å, º)

O1—C5	1.2575 (11)	C4—N4	1.390 (3)
C1—C2^{i}	1.3910 (13)	C5—O1^{i}	1.2575 (11)
C1—C2	1.3910 (13)	N4—H4	0.89 (2)

C1—C5	1.490 (2)	N1—C6	1.3188 (13)
C2—C3	1.3796 (17)	N1—H1A	0.940 (15)
C2—H2	0.9300	N1—H1B	0.875 (16)
C3—C4	1.3886 (15)	N2—C6	1.329 (2)
C3—H3	0.9300	N2—H2A	0.923 (16)
C4—C3ⁱ	1.3886 (15)	C6—N1ⁱ	1.3188 (13)
C2ⁱ—C1—C2	117.65 (14)	O1—C5—O1ⁱ	122.98 (14)
C2ⁱ—C1—C5	121.18 (7)	O1—C5—C1	118.50 (7)
C2—C1—C5	121.18 (7)	O1ⁱ—C5—C1	118.50 (7)
C3—C2—C1	121.34 (11)	C4—N4—H4	113.7 (13)
C3—C2—H2	119.3	C6—N1—H1A	119.5 (8)
C1—C2—H2	119.3	C6—N1—H1B	118.1 (10)
C2—C3—C4	120.50 (12)	H1A—N1—H1B	121.7 (13)
C2—C3—H3	119.7	C6—N2—H2A	115.3 (9)
C4—C3—H3	119.7	N1ⁱ—C6—N1	119.95 (15)
C3—C4—C3ⁱ	118.64 (15)	N1ⁱ—C6—N2	120.02 (8)
C3—C4—N4	120.68 (8)	N1—C6—N2	120.02 (8)
C3ⁱ—C4—N4	120.68 (8)		
C2ⁱ—C1—C2—C3	1.2 (2)	C2ⁱ—C1—C5—O1	−179.70 (13)
C5—C1—C2—C3	−179.36 (12)	C2—C1—C5—O1	0.8 (2)
C1—C2—C3—C4	−0.1 (2)	C2ⁱ—C1—C5—O1ⁱ	−0.8 (2)
C2—C3—C4—C3ⁱ	−1.0 (3)	C2—C1—C5—O1ⁱ	179.70 (13)
C2—C3—C4—N4	179.23 (16)		

Symmetry code: (i) $x, -y+1/2, z$.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1ⁱⁱ	0.940 (15)	1.869 (16)	2.8068 (14)	175.4 (13)
N1—H1B···O1ⁱⁱⁱ	0.875 (16)	2.107 (16)	2.9032 (15)	151.0 (13)
N2—H2A···O1ⁱⁱⁱ	0.923 (16)	2.099 (16)	2.9408 (8)	151.1 (12)

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