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Guanidinium benzoate

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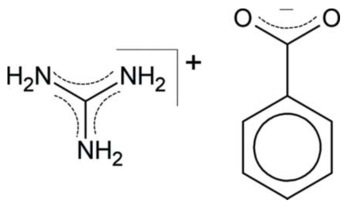
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.035; wR factor = 0.101; data-to-parameter ratio = 12.6.

In the title compound, $C_7H_5O_2^-\cdot CH_6N_3^+$, the cation and anion lie on crystallographic mirror planes. The bond length in the deprotonated carboxyl group is intermediate between normal single and double Csp^2═O bond lengths, indicating delocalization of the charge over both O atoms of the COO$^-$ group. Hydrogen bonds assemble the ions into layers in the *bc* plane.

Related literature

For related literature, see: Allen *et al.* (1987); Zyss *et al.* (1993).



Experimental

Crystal data

$CH_6N_3^+\cdot C_7H_5O_2^-$
M_r = 181.20
Orthorhombic, *Pnma*
a = 15.7347 (8) Å
b = 8.1216 (4) Å
c = 7.8885 (4) Å
V = 1008.08 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 (2) K
0.25 × 0.13 × 0.07 mm

Data collection

Bruker APEX2 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.927, T_{max} = 0.994
27265 measured reflections
960 independent reflections
735 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.101
S = 1.04
960 reflections
76 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.09 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.2519 (13)	C1—N2	1.328 (3)
C1—N1	1.3162 (15)		
O1^i—C2—O1	123.29 (17)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1^{ii}	0.931 (18)	1.902 (19)	2.8309 (17)	175.1 (14)
N2—H2···O1^{iii}	0.915 (18)	2.171 (19)	2.9700 (10)	145.4 (14)
N1—H1B···O1^i	0.860 (17)	2.081 (17)	2.8816 (17)	154.7 (15)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; 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: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2327).

References

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supplementary materials

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Guanidinium benzoate

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Comment

Guanidine is a strong base ($pK_a = 13.5$) and readily reacts with all types of organic acids to give salts with good crystallinity, 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 (Zyss *et al.*, 1993). We are currently engaged in a research project aimed at investigating the structures and dielectric and optical properties of guanidine and guanidine derivative compounds.

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

The benzoate anion is almost in a planar conformation, with a dihedral angle of 0.41 (18)° between the phenyl ring and the carboxylate group.

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 normal 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 $C_{3\ h}$. 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 of the guanidinium cation are involved in N—H···O interactions with the anion (Fig. 2, Table 2) forming layers in the bc plane, each carboxylate O atom accepting three H atoms. In each layer, the cation is bonded to three anions, two approximately perpendicular and one approximately coplanar (Fig. 3).

Experimental

The title compound was prepared by adding benzoic acid (Aldrich 99.5%; 1.1 mmol) to guanidinium carbonate (Aldrich 99%; 0.55 mmol) dissolved in water (60 ml). The solution was warmed slowly and then left to evaporate under ambient conditions. After a few days, small colourless transparent single crystals of (I) were deposited.

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, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

Fig. 1. A plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (a) x, 1/2-y, z; (b) x, 3/2-y, z.]

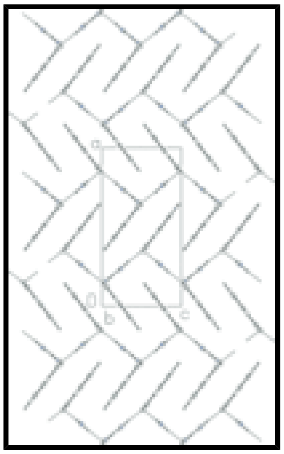

Fig. 2. A packing diagram for (I), viewed down the b axis, showing the layer formation. Hydrogen bonds are shown as dashed lines.

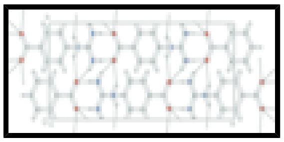

Fig. 3. A packing diagram for (I), viewed down the c axis, with the hydrogen bonds depicted by dashed lines.

Guanidinium benzoate

Crystal data

$CH_6N_3^+ \cdot C_7H_5O_2^-$
$M_r = 181.20$
Orthorhombic, *Pnma*
Hall symbol: -P 2ac 2n
$a = 15.7347$ (8) Å
$b = 8.1216$ (4) Å
$c = 7.8885$ (4) Å
$V = 1008.08$ (9) Å^3
$Z = 4$

$F_{000} = 384$
$D_x = 1.194$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 6505 reflections
$\theta = 2.9$–$23.6°$
$\mu = 0.09$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.25 × 0.13 × 0.07 mm

Data collection

Bruker APEX2 CCD area-detector diffractometer	960 independent reflections
Radiation source: fine-focus sealed tube	735 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\mathrm{int}} = 0.035$
$T = 293(2)$ K	$\theta_{\max} = 25.1°$
φ and ω scans	$\theta_{\min} = 2.6°$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$h = -18 \rightarrow 18$
$T_{\min} = 0.927$, $T_{\max} = 0.994$	$k = -9 \rightarrow 9$
27265 measured reflections	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 0.1512P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$(\Delta/\sigma)_{\max} < 0.001$
$wR(F^2) = 0.101$	$\Delta\rho_{\max} = 0.09$ e Å^{-3}
$S = 1.04$	$\Delta\rho_{\min} = -0.16$ e Å^{-3}
960 reflections	Extinction correction: none
76 parameters	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

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 > 2sigma(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*	$U_{\mathrm{iso}}*/U_{\mathrm{eq}}$
O1	0.14899 (6)	0.11435 (12)	0.01484 (12)	0.0621 (4)
C1	0.21113 (11)	0.7500	0.1719 (2)	0.0487 (5)

C2	0.11899 (11)	0.2500	0.0607 (2)	0.0466 (5)
C3	0.04384 (11)	0.2500	0.1780 (2)	0.0509 (5)
C4	0.00836 (10)	0.1032 (2)	0.2325 (2)	0.0684 (5)
H4	0.0313	0.0038	0.1962	0.082*
C5	−0.06091 (10)	0.1034 (3)	0.3405 (2)	0.0913 (6)
H5	−0.0842	0.0044	0.3773	0.110*
C6	−0.09507 (17)	0.2500	0.3930 (3)	0.0990 (10)
H6	−0.1419	0.2500	0.4650	0.119*
N1	0.23780 (9)	0.60957 (15)	0.23598 (18)	0.0634 (4)
H1A	0.2775 (10)	0.6096 (19)	0.323 (2)	0.076*
H1B	0.2182 (9)	0.521 (2)	0.191 (2)	0.076*
N2	0.15725 (12)	0.7500	0.0424 (2)	0.0648 (5)
H2	0.1368 (10)	0.848 (2)	0.0030 (19)	0.078*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0749 (7)	0.0404 (6)	0.0709 (7)	0.0054 (4)	0.0148 (5)	0.0038 (5)
C1	0.0506 (10)	0.0433 (10)	0.0520 (11)	0.000	−0.0003 (9)	0.000
C2	0.0538 (10)	0.0399 (11)	0.0462 (10)	0.000	−0.0039 (8)	0.000
C3	0.0517 (11)	0.0592 (12)	0.0418 (10)	0.000	−0.0069 (8)	0.000
C4	0.0633 (9)	0.0781 (11)	0.0638 (9)	−0.0054 (7)	0.0006 (7)	0.0148 (8)
C5	0.0696 (11)	0.1285 (17)	0.0757 (12)	−0.0177 (11)	0.0059 (9)	0.0298 (12)
C6	0.0653 (16)	0.170 (3)	0.0618 (16)	0.000	0.0113 (12)	0.000
N1	0.0737 (9)	0.0417 (7)	0.0748 (9)	0.0040 (6)	−0.0205 (7)	−0.0017 (6)
N2	0.0758 (12)	0.0506 (11)	0.0680 (11)	0.000	−0.0234 (10)	0.000

Geometric parameters (Å, °)

O1—C2	1.2519 (13)	C4—H4	0.9300
C1—N1^{i}	1.3162 (15)	C5—C6	1.371 (2)
C1—N1	1.3162 (15)	C5—H5	0.9300
C1—N2	1.328 (3)	C6—C5^{ii}	1.371 (2)
C2—O1^{ii}	1.2519 (13)	C6—H6	0.9300
C2—C3	1.502 (3)	N1—H1A	0.931 (18)
C3—C4	1.3846 (17)	N1—H1B	0.860 (17)
C3—C4^{ii}	1.3846 (17)	N2—H2	0.915 (18)
C4—C5	1.383 (2)		
N1^{i}—C1—N1	120.12 (18)	C3—C4—H4	119.7
N1^{i}—C1—N2	119.94 (9)	C6—C5—C4	119.7 (2)
N1—C1—N2	119.94 (9)	C6—C5—H5	120.1
O1^{ii}—C2—O1	123.29 (17)	C4—C5—H5	120.1
O1^{ii}—C2—C3	118.35 (9)	C5^{ii}—C6—C5	120.6 (2)
O1—C2—C3	118.35 (9)	C5^{ii}—C6—H6	119.7
C4—C3—C4^{ii}	118.83 (19)	C5—C6—H6	119.7
C4—C3—C2	120.58 (10)	C1—N1—H1A	119.9 (10)

C4^{ii}—C3—C2	120.59 (10)	C1—N1—H1B	117.1 (11)
C5—C4—C3	120.54 (17)	H1A—N1—H1B	123.0 (15)
C5—C4—H4	119.7	C1—N2—H2	119.1 (10)

Symmetry codes: (i) *x*, −*y*+3/2, *z*; (ii) *x*, −*y*+1/2, *z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O1^{iii}	0.931 (18)	1.902 (19)	2.8309 (17)	175.1 (14)
N2—H2···O1^{iv}	0.915 (18)	2.171 (19)	2.9700 (10)	145.4 (14)
N1—H1B···O1^{ii}	0.860 (17)	2.081 (17)	2.8816 (17)	154.7 (15)

Symmetry codes: (iii) −*x*+1/2, *y*+1/2, *z*+1/2; (iv) *x*, *y*+1, *z*; (ii) *x*, −*y*+1/2, *z*.

Fig. 1

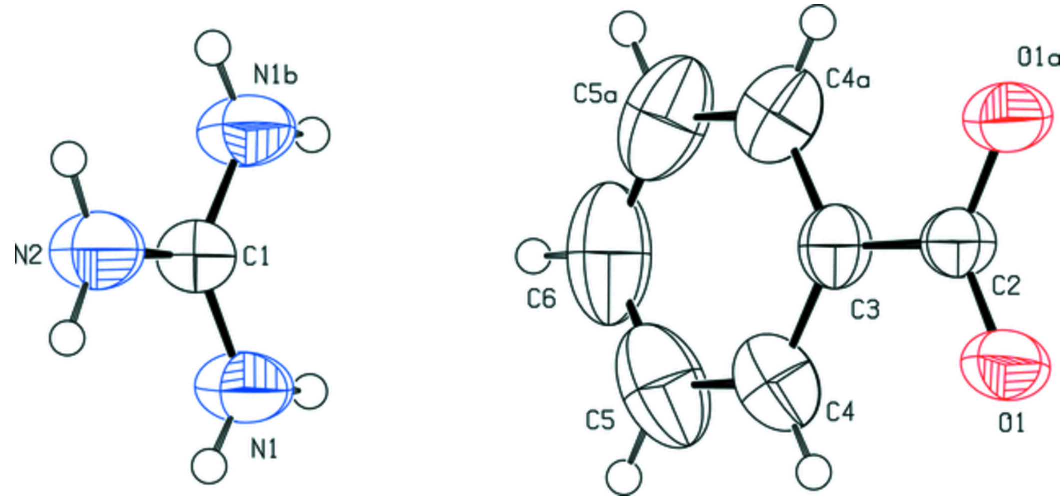

Fig. 2

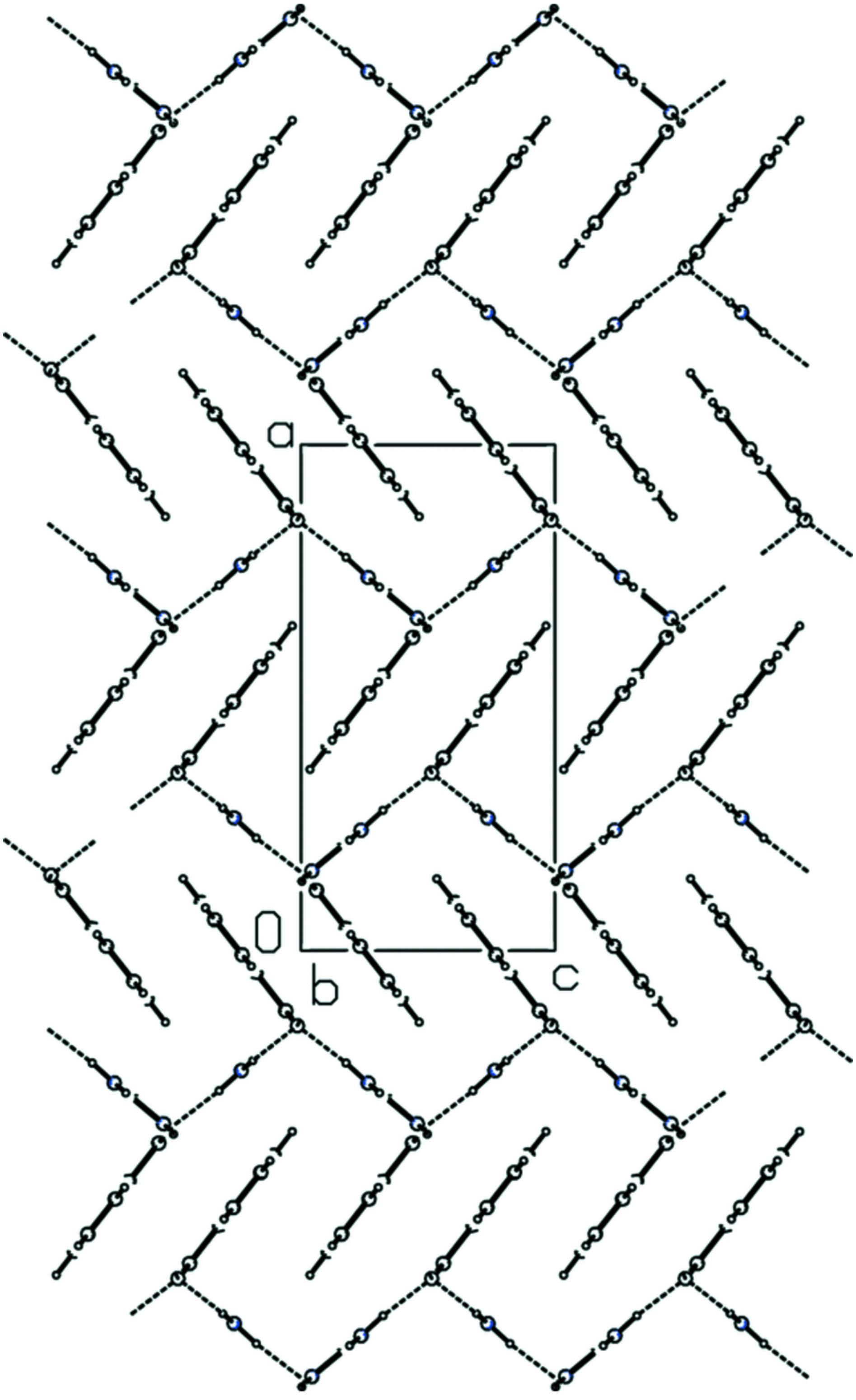

Fig. 3