

## 2-Carboxy-1-(3-nitrophenyl)-ethaniminium perchlorate

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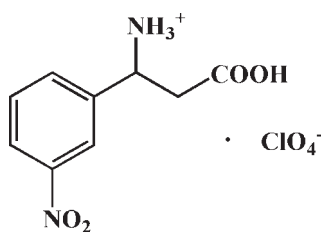
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  
R factor = 0.058; wR factor = 0.237; data-to-parameter ratio = 15.3.

In the cation of the title compound,  $\text{C}_9\text{H}_{11}\text{N}_2\text{O}_4^+\cdot\text{ClO}_4^-$ , the conformation is stabilized by an intramolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bond. In the crystal packing, centrosymmetrically related cations interact through intermolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds involving the carboxy groups, forming dimers. The dimers and the perchlorate anions are further linked into layers parallel to the  $ab$  plane by  $\text{C}-\text{H}\cdots\text{O}$  and  $\text{N}-\text{H}\cdots\text{O}$  hydrogen-bonding interactions.

## Related literature

For the synthesis of  $\beta$ -amino acids, see: Cohen *et al.* (2002); Qu *et al.* (2004); Zhao (2007). For hydrogen-bond motifs, see: Bernstein *et al.* (1995); Etter *et al.* (1990).



## Experimental

## Crystal data

$\text{C}_9\text{H}_{11}\text{N}_2\text{O}_4^+\cdot\text{ClO}_4^-$   
 $M_r = 310.65$   
Triclinic,  $P\bar{1}$   
 $a = 7.5932$  (8) Å  
 $b = 7.8843$  (1) Å  
 $c = 11.8615$  (6) Å  
 $\alpha = 94.745$  (3)°  
 $\beta = 99.780$  (7)°

$\gamma = 116.323$  (4)°  
 $V = 617.11$  (7) Å<sup>3</sup>  
 $Z = 2$   
Mo  $K\alpha$  radiation  
 $\mu = 0.35$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.45 \times 0.30 \times 0.15$  mm

## Data collection

Rigaku SCXmini diffractometer  
Absorption correction: multi-scan  
(*CrystalClear*; Rigaku, 2005)  
 $T_{\min} = 0.884$ ,  $T_{\max} = 0.950$

6395 measured reflections  
2799 independent reflections  
1732 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.049$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$   
 $wR(F^2) = 0.237$   
 $S = 0.99$   
2799 reflections

183 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.58$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.53$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2A}\cdots\text{O4}$	0.89	2.36	2.953 (4)	124
$\text{N2}-\text{H2A}\cdots\text{O8}$	0.89	2.15	2.884 (5)	139
$\text{N2}-\text{H2B}\cdots\text{O5}^i$	0.89	2.31	3.113 (5)	150
$\text{N2}-\text{H2B}\cdots\text{O6}^i$	0.89	2.34	3.120 (5)	147
$\text{N2}-\text{H2C}\cdots\text{O2}^{ii}$	0.89	2.15	2.960 (5)	152
$\text{O3}-\text{H3}\cdots\text{O4}^{iii}$	0.82	1.89	2.690 (4)	167
$\text{C2}-\text{H2}\cdots\text{O8}^{iv}$	0.93	2.58	3.420 (5)	150
$\text{C6}-\text{H6}\cdots\text{O2}^{ii}$	0.93	2.54	3.445 (5)	163
$\text{C8}-\text{H8A}\cdots\text{O6}^{iv}$	0.97	2.50	3.403 (5)	154
$\text{C8}-\text{H8B}\cdots\text{O7}^v$	0.97	2.57	3.134 (6)	117

Symmetry codes: (i)  $-x + 1, -y, -z + 1$ ; (ii)  $x - 1, y - 1, z$ ; (iii)  $-x, -y + 1, -z + 1$ ; (iv)  $-x + 1, -y + 1, -z + 1$ ; (v)  $-x, -y, -z + 1$ .

Data collection: *CrystalClear* (Rigaku 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *PRPKAPPA* (Ferguson, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2399).

## References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.  
Cohen, J. H., Abdel-Magid, A. F., Almond, H. R. Jr & Maryanoff, C. A. (2002). *Tetrahedron Lett.* **43**, 1977–1981.  
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.  
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.  
Qu, Z.-R., Zhao, H., Wang, Y.-P., Wang, X.-S., Ye, Q., Li, Y.-H., Xiong, R.-G., Abrahams, B. F., Liu, Z.-G. & Xue, Z.-L. (2004). *Chem. Eur. J.* **10**, 54–60.  
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.  
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
Zhao, H. (2007). *Acta Cryst.* **E63**, o3400.

**supplementary materials**

*Acta Cryst.* (2010). E66, o117 [ doi:10.1107/S1600536809051319 ]

## 2-Carboxy-1-(3-nitrophenyl)ethanaminium perchlorate

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### Comment

$\beta$ -Amino acids are important molecules due to their pharmacological properties. Recently, there have been an increased interest in the enantiomeric preparation of  $\beta$ -amino acids as precursors for the synthesis of novel biologically active compounds (Cohen *et al.*, 2002). In addition,  $\beta$ -amino acids are attractive ligands for use in the generation of polar coordination polymers, especially when one considers that the ferroelectric compounds (Qu *et al.*, 2004).

The asymmetric unit of the title compound (Fig. 1) contains one 1-(3-nitrophenyl)-2-carboxyethanaminium and one perchlorate anion. The conformation of the cation is stabilized by an intramolecular N—H $\cdots$ O hydrogen bond (Table 1). In the crystal packing, centrosymmetrically related cations at (x, y, z) and (-x, 1-y, 1-z) are linked into a dimer by intermolecular O—H $\cdots$ O hydrogen bonds involving the carboxy groups forming an eighth-membered ring of graph set motif  $R^2_2(8)$  (Etter *et al.*, 1990; Bernstein *et al.*, 1995). The dimers and the perchlorate anions are further connected into layers parallel to the *ab* plane (Fig. 2) by C—H $\cdots$ O and N—H $\cdots$ O hydrogen bonding interactions.

### Experimental

Under nitrogen protection, 3-nitrobenzaldehyde (4.53 g, 30 mmol), malonic acid (5.0 g, 48 mmol) and ammonium acetate (6.0 g, 78 mmol) were added in a flask and refluxed for 12 h yielding a white precipitate. After being cooled to room temperature, the solution was filtered, and the 3-amino-3-(3-nitrophenyl)propanoic acid obtained was dissolved in ethanol and perchloric acid. After slow evaporation of the solution over a period of 3 d, colourless prismatic crystals of the title compound suitable for X-ray diffraction analysis were isolated.

### Refinement

All H atoms were calculated geometrically and were allowed to ride on their parent atoms, with C—H = 0.93–0.97 Å, N—H = 0.89 Å, O—H = 0.82 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$  or  $1.5 U_{\text{eq}}(\text{N}, \text{O})$ .

### Figures

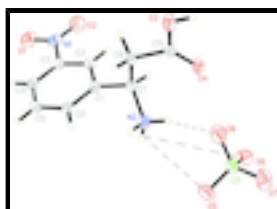


Fig. 1. The asymmetric unit in the title compound, with the displacement ellipsoids were drawn at the 30% probability level. Intramolecular hydrogen bonds are shown as dashed lines.

## 2-Carboxy-1-(3-nitrophenyl)ethanaminium perchlorate

### Crystal data

$C_9H_{11}N_2O_4^+ \cdot ClO_4^-$	$Z = 2$
$M_r = 310.65$	$F(000) = 320$
Triclinic, $P\bar{1}$	$D_x = 1.672 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 7.5932 (8) \text{ \AA}$	Cell parameters from 1641 reflections
$b = 7.8843 (1) \text{ \AA}$	$\theta = 3.1\text{--}27.5^\circ$
$c = 11.8615 (6) \text{ \AA}$	$\mu = 0.35 \text{ mm}^{-1}$
$\alpha = 94.745 (3)^\circ$	$T = 293 \text{ K}$
$\beta = 99.780 (7)^\circ$	Prism, colourless
$\gamma = 116.323 (4)^\circ$	$0.45 \times 0.30 \times 0.15 \text{ mm}$
$V = 617.11 (7) \text{ \AA}^3$	

### Data collection

Rigaku SCXmini diffractometer	2799 independent reflections
Radiation source: fine-focus sealed tube graphite	1732 reflections with $I > 2\sigma(I)$
Detector resolution: $13.6612 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.049$
CCD Profile fitting scans	$\theta_{\text{max}} = 27.5^\circ$ , $\theta_{\text{min}} = 2.9^\circ$
Absorption correction: multi-scan ( <i>CrystalClear</i> ; Rigaku, 2005)	$h = -9 \rightarrow 9$
$T_{\text{min}} = 0.884$ , $T_{\text{max}} = 0.950$	$k = -10 \rightarrow 10$
6395 measured reflections	$l = -15 \rightarrow 15$

### Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.058$	H-atom parameters constrained
$wR(F^2) = 0.237$	$w = 1/[\sigma^2(F_o^2) + (0.1426P)^2]$
$S = 0.99$	where $P = (F_o^2 + 2F_c^2)/3$
2799 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
183 parameters	$\Delta\rho_{\text{max}} = 0.58 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.53 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: <i>SHELXL</i>
	Extinction coefficient: $0.0014 (1)$

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.34320 (15)	0.01534 (15)	0.65117 (8)	0.0463 (4)
O5	0.3304 (6)	-0.1381 (5)	0.5737 (3)	0.0772 (11)
O6	0.5400 (5)	0.1058 (5)	0.7279 (3)	0.0763 (11)
O7	0.1979 (6)	-0.0555 (6)	0.7205 (3)	0.0867 (13)
O8	0.3233 (9)	0.1574 (7)	0.5920 (3)	0.0996 (16)
O4	0.1696 (4)	0.4174 (4)	0.4775 (2)	0.0423 (7)
O3	0.0141 (5)	0.5359 (5)	0.3563 (2)	0.0523 (8)
H3	-0.0234	0.5592	0.4138	0.079*
C3	0.7013 (5)	0.4845 (5)	0.1024 (3)	0.0343 (8)
C2	0.6238 (5)	0.4860 (5)	0.1994 (3)	0.0346 (8)
H2	0.6888	0.5908	0.2602	0.042*
C1	0.4454 (5)	0.3264 (5)	0.2039 (3)	0.0315 (7)
N1	0.8866 (5)	0.6592 (5)	0.0985 (3)	0.0467 (9)
N2	0.2618 (5)	0.1458 (5)	0.3442 (3)	0.0444 (8)
H2A	0.2265	0.1591	0.4110	0.067*
H2B	0.3490	0.0984	0.3536	0.067*
H2C	0.1525	0.0659	0.2896	0.067*
C9	0.1278 (5)	0.4556 (5)	0.3827 (3)	0.0345 (8)
C7	0.3587 (5)	0.3383 (5)	0.3081 (3)	0.0338 (8)
H7	0.4696	0.4278	0.3728	0.041*
C6	0.3520 (5)	0.1742 (5)	0.1112 (3)	0.0366 (8)
H6	0.2322	0.0683	0.1136	0.044*
O1	0.9505 (5)	0.6627 (5)	0.0093 (3)	0.0696 (10)
C5	0.4334 (6)	0.1763 (6)	0.0143 (3)	0.0386 (8)
H5	0.3682	0.0730	-0.0475	0.046*
O2	0.9618 (5)	0.7907 (5)	0.1799 (3)	0.0722 (10)
C4	0.6139 (6)	0.3347 (6)	0.0106 (3)	0.0394 (9)
H4	0.6728	0.3382	-0.0524	0.047*
C8	0.2089 (6)	0.4171 (6)	0.2816 (3)	0.0370 (8)
H8A	0.2741	0.5361	0.2528	0.044*
H8B	0.0960	0.3263	0.2198	0.044*

## supplementary materials

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### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.0496 (6)	0.0469 (6)	0.0457 (6)	0.0250 (5)	0.0138 (4)	0.0040 (4)
O5	0.077 (3)	0.055 (2)	0.092 (3)	0.0231 (19)	0.034 (2)	-0.0077 (19)
O6	0.054 (2)	0.071 (2)	0.082 (2)	0.0171 (19)	-0.0018 (18)	0.013 (2)
O7	0.062 (2)	0.103 (3)	0.084 (3)	0.023 (2)	0.040 (2)	0.002 (2)
O8	0.185 (5)	0.119 (3)	0.047 (2)	0.119 (4)	0.017 (2)	0.022 (2)
O4	0.0490 (15)	0.0624 (18)	0.0341 (14)	0.0396 (15)	0.0155 (12)	0.0111 (12)
O3	0.0618 (18)	0.086 (2)	0.0394 (14)	0.0580 (18)	0.0179 (14)	0.0155 (15)
C3	0.0284 (17)	0.041 (2)	0.0417 (19)	0.0200 (16)	0.0139 (15)	0.0149 (16)
C2	0.0292 (18)	0.0376 (19)	0.0381 (19)	0.0168 (16)	0.0071 (15)	0.0057 (15)
C1	0.0296 (17)	0.0360 (18)	0.0319 (17)	0.0174 (15)	0.0082 (14)	0.0056 (14)
N1	0.0353 (18)	0.049 (2)	0.065 (2)	0.0217 (17)	0.0210 (17)	0.0245 (19)
N2	0.056 (2)	0.052 (2)	0.0401 (17)	0.0335 (18)	0.0215 (16)	0.0162 (15)
C9	0.0336 (18)	0.0391 (19)	0.0350 (18)	0.0198 (16)	0.0111 (15)	0.0045 (15)
C7	0.0297 (17)	0.0371 (19)	0.0349 (18)	0.0149 (15)	0.0101 (14)	0.0070 (15)
C6	0.0341 (18)	0.0330 (18)	0.0413 (19)	0.0137 (16)	0.0119 (15)	0.0046 (15)
O1	0.062 (2)	0.080 (2)	0.088 (2)	0.0352 (19)	0.053 (2)	0.041 (2)
C5	0.042 (2)	0.040 (2)	0.0376 (19)	0.0215 (18)	0.0115 (16)	0.0028 (16)
O2	0.055 (2)	0.054 (2)	0.074 (2)	-0.0025 (17)	0.0133 (18)	0.0074 (19)
C4	0.043 (2)	0.056 (2)	0.0359 (18)	0.032 (2)	0.0193 (16)	0.0173 (17)
C8	0.043 (2)	0.045 (2)	0.0356 (18)	0.0273 (18)	0.0198 (16)	0.0116 (16)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

C11—O5	1.414 (3)	N1—O1	1.234 (4)
C11—O8	1.419 (4)	N2—C7	1.501 (5)
C11—O7	1.429 (4)	N2—H2A	0.8900
C11—O6	1.433 (4)	N2—H2B	0.8900
O4—C9	1.214 (4)	N2—H2C	0.8900
O3—C9	1.292 (4)	C9—C8	1.506 (4)
O3—H3	0.8200	C7—C8	1.521 (5)
C3—C4	1.366 (5)	C7—H7	0.9800
C3—C2	1.380 (5)	C6—C5	1.392 (5)
C3—N1	1.481 (5)	C6—H6	0.9300
C2—C1	1.395 (5)	C5—C4	1.397 (5)
C2—H2	0.9300	C5—H5	0.9300
C1—C6	1.384 (5)	C4—H4	0.9300
C1—C7	1.511 (5)	C8—H8A	0.9700
N1—O2	1.207 (5)	C8—H8B	0.9700
O5—C11—O8	111.9 (2)	O4—C9—O3	125.3 (3)
O5—C11—O7	110.5 (2)	O4—C9—C8	122.8 (3)
O8—C11—O7	111.6 (3)	O3—C9—C8	111.9 (3)
O5—C11—O6	107.7 (2)	N2—C7—C1	111.0 (3)
O8—C11—O6	107.2 (3)	N2—C7—C8	111.1 (3)
O7—C11—O6	107.7 (2)	C1—C7—C8	110.1 (3)

C9—O3—H3	109.5	N2—C7—H7	108.2
C4—C3—C2	123.7 (3)	C1—C7—H7	108.2
C4—C3—N1	119.4 (3)	C8—C7—H7	108.2
C2—C3—N1	116.9 (3)	C1—C6—C5	121.4 (3)
C3—C2—C1	118.3 (3)	C1—C6—H6	119.3
C3—C2—H2	120.9	C5—C6—H6	119.3
C1—C2—H2	120.9	C6—C5—C4	119.4 (3)
C6—C1—C2	119.1 (3)	C6—C5—H5	120.3
C6—C1—C7	124.0 (3)	C4—C5—H5	120.3
C2—C1—C7	116.7 (3)	C3—C4—C5	117.9 (3)
O2—N1—O1	124.1 (4)	C3—C4—H4	121.0
O2—N1—C3	118.7 (3)	C5—C4—H4	121.0
O1—N1—C3	117.1 (4)	C9—C8—C7	115.3 (3)
C7—N2—H2A	109.5	C9—C8—H8A	108.4
C7—N2—H2B	109.5	C7—C8—H8A	108.4
H2A—N2—H2B	109.5	C9—C8—H8B	108.4
C7—N2—H2C	109.5	C7—C8—H8B	108.4
H2A—N2—H2C	109.5	H8A—C8—H8B	107.5
H2B—N2—H2C	109.5		

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A $\cdots$ O4	0.89	2.36	2.953 (4)	124
N2—H2A $\cdots$ O8	0.89	2.15	2.884 (5)	139
N2—H2B $\cdots$ O5 <sup>i</sup>	0.89	2.31	3.113 (5)	150
N2—H2B $\cdots$ O6 <sup>i</sup>	0.89	2.34	3.120 (5)	147
N2—H2C $\cdots$ O2 <sup>ii</sup>	0.89	2.15	2.960 (5)	152
O3—H3 $\cdots$ O4 <sup>iii</sup>	0.82	1.89	2.690 (4)	167
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Fig. 1

