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L-Citrullinium perchlorate

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Key indicators

Single-crystal X-ray study
T = 105 K
Mean σ(C–C) = 0.001 Å
R factor = 0.023
wR factor = 0.068
Data-to-parameter ratio = 32.1

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

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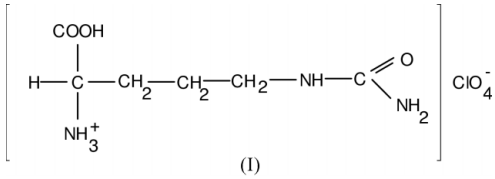
In the title compound, $C_6H_{14}N_3O_3^+\cdot ClO_4^-$, the citrullinium residue forms a strong O—H···O hydrogen bonds with the terminal O atom of a symmetry-related residue. This residue has a *gauche* I-*trans-trans-trans* conformation. The crystal structure is stabilized by an N—H···O hydrogen-bonding network. The perchlorate anion is linked to the cation, forming chains along the *a* axis.

Comment

Citrulline amino acid is found in the urea cycle. The crystal structures of L-citrulline hydrochloride (Naganathan & Venkatesan, 1971), L-citrulline hydrochloride and L-homocitrulline hydrochloride (Ashida *et al.*, 1972), and L-citrulline (Toffoli *et al.*, 1987) have been reported. In the present study, the crystal structure determination of L-citrullinium perchlorate, (I), was undertaken.



(I)

The asymmetric unit of the unit cell of (I) contains a citrullinium cation and a perchlorate anion (Fig. 1). The unsymmetrical C—O bond distances [1.2189 (8) and 1.3151 (8) Å] and the O—C—C bond angles [122.81 (6) and 111.63 (5)°] clearly confirm the protonation of the carboxyl group. Generally, the citrulline residue has three planar groups, *viz*. the carboxyl group, the aliphatic group and the carbamylamino group or urea unit (Naganathan & Venkatesan, 1971). The backbone conformation angle ψ^1 (O1*A*—C1—C2—N1) indicates a *cis* conformation [7.52 (8)°]. The deviation of the α-amino N atom from the mean carboxyl plane is 0.149 (1) Å. This tendency to twist about the C—N bond is found in various amino acids (Lakshminarayanan *et al.*, 1967). The straight-chain conformation angle χ^1 (N1—C2—C3—C4) is *gauche* I [68.99 (7)°], while χ^2 (C2—C3—C4—C5) is *trans* [−177.39 (6)°]. The other two conformation angles χ^3 (C3—C4—C5—N2) and χ^4 (C4—C5—N2—C6) are also both *trans* [−179.47 (6) and 162.71 (7)°]. The conformation angles χ^{51} (C5—N2—C6—O1C) and χ^{52} (C5—N2—C6—N3) are 174.51 (6) and −4.72 (11)°, respectively. The aliphatic chain has a fully extended planar conformation (Table 1).

The average Cl—O bond distances and O—Cl—O bond angles are 1.4450 (6) and 109.47 (4)°, respectively, confirming a nearly tetrahedral symmetry. The perchlorate anion plays a vital role in hydrogen bonding, stabilizing the crystal structure.

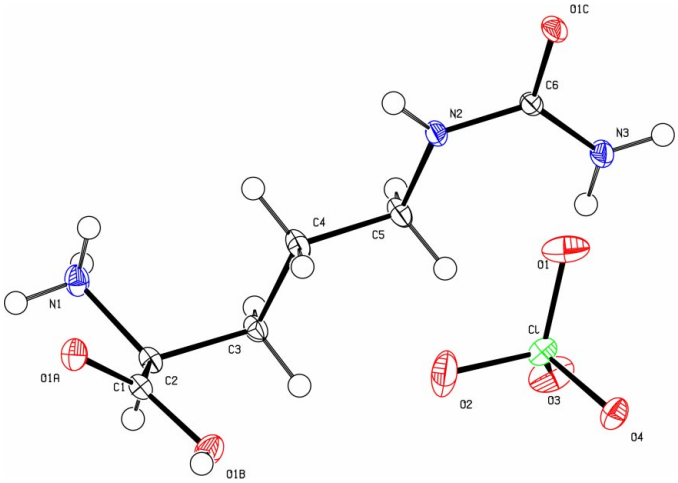


Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).

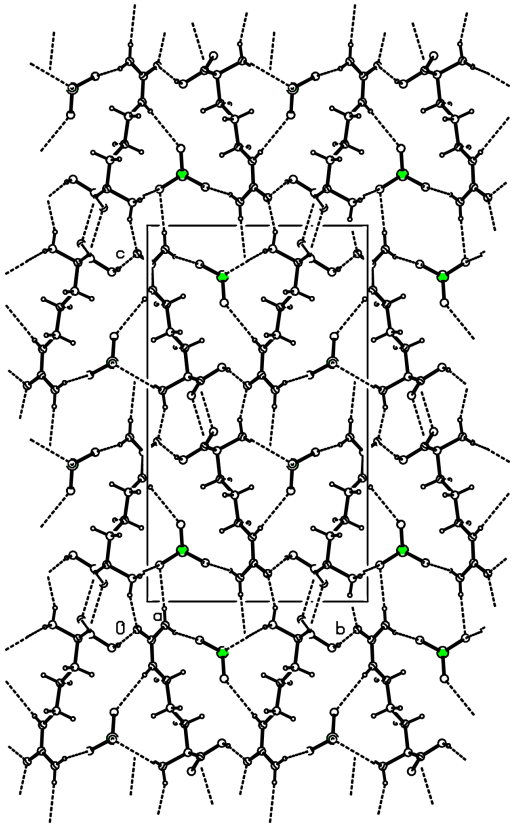


Figure 2
Packing diagram of (I), viewed down the *a* axis.

The carboxyl O atom of the citrulline residue forms a strong O—H···O hydrogen bond with the terminal O atom of a symmetry-related residue (Table 2). The α-, ε- and η-N atoms (N1, N2 and N3) of the citrullinium residue form N—H···O hydrogen bonds with the O atoms of the perchlorate anion. In addition, the α-N atom forms an intermolecular N—H···O hydrogen bond with the terminal O atoms (Fig. 3). A class I hydrogen-bonding pattern is observed in the present structure,

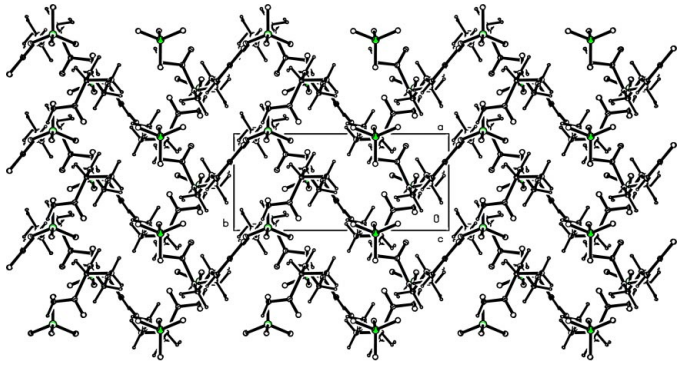


Figure 3
Packing diagram of (I), viewed down the *c* axis. H atoms have been omitted for clarity.

having three two-center hydrogen bonds (Jeffrey & Saenger, 1991). Atom O4 of the perchlorate anion links the citrullinium residues through N^{α}—H···O hydrogen bonds in a chain running along the *a* axis [$O4^{i}\cdots H1A-N1-H1B\cdots O4^{ii}$; symmetry codes: (i) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, y+1/2, -z+\frac{1}{2}$]. The citrullinium residues are packed as corrugated sheets in the *ab* plane, interconnected by O—H···O hydrogen bonding (Fig. 3).

Experimental

The title compound was crystallized by slow evaporation from an aqueous solution of citrulline and perchloric acid in a stoichiometric ratio of 1:1.

Crystal data

$C_6H_{14}N_3O_3^+\cdot ClO_4^-$
$M_r = 275.65$
Orthorhombic, $P2_12_12_1$
$a = 5.1113\ (1)$ Å
$b = 11.3497\ (2)$ Å
$c = 19.3853\ (3)$ Å
$V = 1124.57\ (3)$ Å^3
$Z = 4$
$D_x = 1.628$ Mg m^{-3}
$D_m = 1.615$ Mg m^{-3}
D_m measured by flotation in a mixture of carbon tetrachloride and xylene
Mo $K\alpha$ radiation
Cell parameters from 7473 reflections
$\theta = 2.1$–$37.5°$
$\mu = 0.37$ mm^{-1}
$T = 105\ (2)$ K
Block, colorless
0.70 × 0.45 × 0.30 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.77$, $T_{max} = 0.89$
25355 measured reflections
5866 independent reflections
5757 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 37.5°$
$h = -8 \rightarrow 8$
$k = -19 \rightarrow 18$
$l = -32 \rightarrow 33$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.068$
$S = 1.03$
5866 reflections
183 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 0.1185P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0217 (18)
Absolute structure: Flack (1983)
Flack parameter = 0.02 (3)

Table 1
Selected geometric parameters (Å, °).

O1*A*—C1	1.2189 (8)	O1*B*—C1	1.3151 (8)
O1*A*—C1—C2—N1	7.52 (8)	C4—C5—N2—C6	162.71 (7)
N1—C2—C3—C4	68.99 (7)	C5—N2—C6—O1C	174.51 (6)
C2—C3—C4—C5	−177.39 (6)	C5—N2—C6—N3	−4.72 (11)
C3—C4—C5—N2	−179.47 (6)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*B*—H1···O1*C*^{i}	0.70 (2)	1.84 (2)	2.5292 (8)	171 (2)
N1—H1*A*···O4^{ii}	0.846 (17)	2.234 (17)	3.0226 (9)	155 (2)
N1—H1*B*···O4^{iii}	0.926 (15)	2.162 (16)	2.9699 (9)	145 (1)
N1—H1*C*···O1*C*^{iv}	0.918 (15)	1.906 (15)	2.7986 (8)	164 (1)
N2—H2*A*···O2^{iii}	0.837 (15)	2.583 (14)	3.3562 (10)	154 (1)
N3—H3*C*···O4^{v}	0.818 (13)	2.326 (13)	3.1205 (8)	164 (1)
N3—H3*D*···O1^{vi}	0.833 (15)	2.292 (15)	3.0952 (9)	162 (1)

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

All H atoms were located from a difference Fourier map. Those on the N and O atoms were refined freely, but the remainder were placed in idealized positions and were refined as riding on their parent atoms. 2484 Fridel pairs were measured and used.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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References

Ashida, T., Funakoshi, K., Tsukihara, T., Ueki, T. & Kakudo, M. (1972). *Acta Cryst.* B**28**, 1367–1374.
Bruker (1998). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Jeffrey, G. A. & Saenger, W. (1991). *Hydrogen Bonding in Biological Structures*. Berlin, Heidelberg, New York: Springer-Verlag.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lakshminarayanan, A. V., Sashisekaran, V. & Ramachandran, G. N. (1967). In *Conformation of Biopolymers*, edited by G. N. Ramachandran. London: Academic Press.
Naganathan, P. S. & Venkatesan, K. (1971). *Acta Cryst.* B**27**, 1079–1085.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Spek, A. L. (1999). *PLATON* for Windows. Utrecht University, The Netherlands.
Toffoli, P., Khodadad, P., Rodier, N. & Astoin, J. (1987). *Acta Cryst.* C**43**, 945–947.