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L-Argininium dinitrate

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In the title compound, $C_6H_{16}N_4O_2{}^{2+}\cdot 2NO_3{}^-$, the diprotonated argininium molecule is linked by a strong O—H⋯O [2.653 (7) Å] hydrogen bond to the nitrate anion. The single-bonded O atom of the carboxyl group exhibits a very unusual *cis* conformation with respect to the α-amino N atom. Chelated three-centered hydrogen bonds are observed in the case of the N^α and N^ε atoms with the nitrate anions. The argininium molecules are connected by type *A*, *B* and *D* interactions through nitrate anions.

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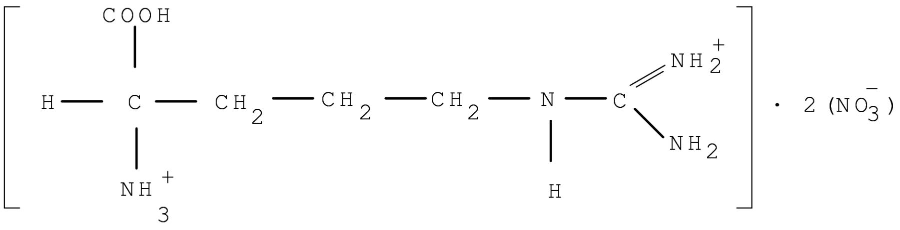
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.010 Å
R factor = 0.070
wR factor = 0.218
Data-to-parameter ratio = 7.1

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

Comment

L-Arginine is one of the essential amino acids widely distributed in biological substances. L-Arginine phosphate monohydrate is found to exhibit interesting non-linear optical properties (Jiang *et al.*, 1983). The strong basicity of the guanidyl group is responsible for the functions in living matter (Aoki *et al.*, 1971). The crystal structures of L-arginine dihydrate (Karle & Karle, 1964), L-arginine hydrochloride monohydrate (Dow *et al.*, 1970), L-arginine phosphate monohydrate (Aoki *et al.*, 1971), L-arginine perchlorate (Monaco *et al.*, 1987; Srinivasan & Rajaram, 1997) and L-arginine diarsenate (Zalkin *et al.*, 1989) have been reported. In the present study, the crystal structure of L-arginine dinitrate, (I), was undertaken to study conformational aspects.



$$\left[\mathrm{H-\underset{NH_3^+}{\overset{COOH}{C}}-CH_2-CH_2-CH_2-\underset{H}{N}-C\begin{matrix}\mathrm{=NH_2^+}\\ \mathrm{-NH_2}\end{matrix}}\right]\cdot 2\,(\mathrm{NO_3^-})$$

(I)

The conformation of the arginine molecule may be characterized by three planar groups: (i) the carboxyl group, (ii) the side chain C atoms consisting of the α-, β-, γ- and δ-carbon (C12, C13, C14 and C15) and (iii) the guanidyl group including the δ-C atom (C15, N4, C16, N5 and N6) (Aoki *et al.*, 1971). The conformation of the single-bonded carboxyl O atom is *cis* with respect to the amino N atom [−29.7 (10)°] for the diprotonated argininium molecule. In general, this conformation is found to be *trans*, whereas the present structure is different from earlier studies, *viz*. L-valine hydrochloride (Koetzle *et al.*, 1974), DL-valine hydrochloride (Di Blasio *et al.*, 1977), L-arginine diarsenate (Zalkin *et al.*, 1989), bis(DL-methioninium) sulfate (Srinivasan *et al.*, 2001), tri(L-isoleuci-

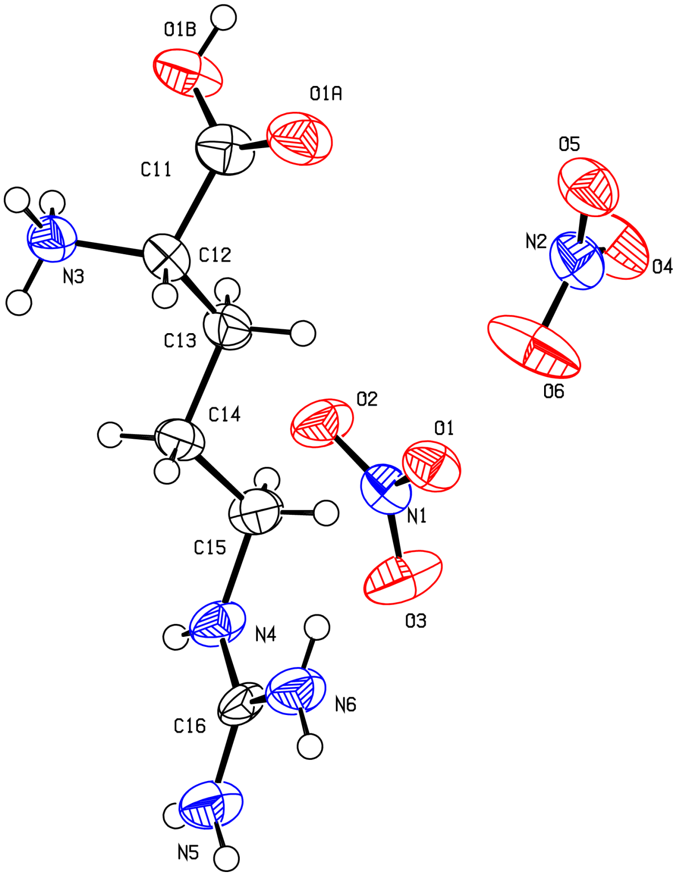


Figure 1
The molecular structure of the diprotonated argininium cation showing the atomic numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).

nium) sulfate bisulfate (Sridhar *et al.*, 2001) and L-valine L-valinium perchlorate monohydrate (Pandiarajan *et al.*, 2001).

The side-chain conformation angle χ^1 has a *gauche* II form [−62.5 (8)°], while χ^2 and χ^3 are in the *trans* form [−168.6 (6) and 178.0 (6)°] for the argininium molecule (Fig. 1). The other conformation angle, which has the guanidyl group at the end of the residue, χ^4 [−92.9 (10)°], is as expected and χ^{51} and χ^{52} are 6.6 (14) and −172.6 (8)°, respectively. These conformational angles are very similar to those on L-arginine diarsenate, except for χ^4 which is 148.8°. The argininium molecule, in the present study, is in a slightly folded conformation.

The guanidyl group is protonated and exists as a guanidinium ion. The three C—N bonds in this group are nearly equal in length with an average value of 1.313 (9) Å. The three N—C—N angles are very close to 120°, confirming the planarity of the guanidyl group. Like other arginine molecules, the C15 atom is only slightly displaced [0.15 (2) Å] from the plane of the guanidyl group. The two crystallographically independent nitrate anions have similar geometries.

The carboxyl O atom of the diprotonated argininium cation is linked through a strong O—H···O hydrogen bond [2.653 (7) Å] with the nitrate anion (Table 2), while the amino-N and the N atoms of the guanidyl group are linked through normal hydrogen bonds with the two nitrate anions. Chelated three-centered hydrogen bonds are observed in the case of the N^{α} and N^{ε} atoms (N3—H3C···O5^{ii} and N3—H3C···O4^{ii}, and N4—H4···O3^{iii} and N4—H4···O2^{iii}; Jeffrey & Saenger, 1991). The O atom (O2) of the nitrate anion links the carboxyl O atom (O1*B*), N^{ε} and $N^{\eta1}$ (N5) through a chain along the *c* axis. The O atoms of the second nitrate anion (O5 and O4) link the α-amino N atom and $N^{\eta2}$ (N6) through a chain along the *a* axis. The intermolecular guanidyl–nitrate interactions are observed as (i) type *D* between N atoms ε, $\eta1$ with O2; (ii) type *A* between N atoms $\eta1$, $\eta2$ with O3 and O1 and (iii) type *B* between N atoms ε, $\eta1$ with O3 and O2 of the nitrate anions (Salunke & Vijayan, 1981). An intermolecular short contact of 2.903 (12) Å is observed between O4 and the carboxyl C11($1-x, \frac{1}{2}+y, 1-z$) atom.

Experimental

The title compound was crystallized in aqueous solution from a 1:2 stoichiometric ratio of L-arginine and nitric acid. Colorless needle-shaped crystals were grown.

Crystal data

$C_6H_{16}N_4O_2^{2+}\cdot 2NO_3^-$
$M_r = 300.25$
Monoclinic, $P2_1$
$a = 7.744$ (5) Å
$b = 7.284$ (5) Å
$c = 11.653$ (5) Å
$\beta = 92.600$ (5)°
$V = 656.6$ (7) Å^3
$Z = 2$
$D_x = 1.519$ Mg m^{-3}
$D_m = 1.519$ Mg m^{-3}
D_m measured by flotation in a mixture of carbon tetrachloride and xylene
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 14.9$–26.9°
$\mu = 1.22$ mm^{-1}
$T = 293$ (2) K
Needle, colorless
0.03 × 0.02 × 0.01 mm

Data collection

Enraf–Nonius sealed-tube diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.967$, $T_{max} = 0.984$
1284 measured reflections
1284 independent reflections
1213 reflections with $I > 2\sigma(I)$
$\theta_{max} = 68.0°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 14$
3 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.218$
$S = 1.08$
1284 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1*A*—C11	1.201 (9)	C16—N6	1.308 (9)
O1*B*—C11	1.320 (8)	C16—N5	1.336 (9)
N4—C16	1.296 (9)		
N4—C16—N6	122.5 (6)	N6—C16—N5	118.0 (6)
N4—C16—N5	119.4 (6)		
O1*B*—C11—C12—N3	−29.7 (10)	C14—C15—N4—C16	−92.9 (10)
N3—C12—C13—C14	−62.5 (8)	C15—N4—C16—N6	6.6 (14)
C12—C13—C14—C15	−168.6 (6)	C15—N4—C16—N5	−172.6 (8)
C13—C14—C15—N4	178.0 (6)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*B*—H1*B*···O2$^{\rm i}$	0.82	1.85	2.653 (7)	166
N3—H3*A*···O1	0.89	2.08	2.950 (8)	165
N3—H3*B*···O5	0.89	1.94	2.823 (9)	170
N3—H3*C*···O5$^{\rm ii}$	0.89	2.00	2.855 (9)	161
N3—H3*C*···O4$^{\rm ii}$	0.89	2.49	3.212 (9)	139
N4—H4···O3$^{\rm iii}$	0.86	2.22	3.010 (8)	153
N4—H4···O2$^{\rm iii}$	0.86	2.36	3.138 (8)	151
N5—H5*A*···O2$^{\rm iii}$	0.86	2.34	3.086 (9)	146
N5—H5*B*···O1$^{\rm iv}$	0.86	2.17	3.022 (8)	173
N6—H6*A*···O4$^{\rm v}$	0.86	2.18	2.998 (9)	158
N6—H6*B*···O3$^{\rm iv}$	0.86	2.10	2.957 (9)	177

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; 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

Aoki, K., Nagano, K. & Iitaka, Y. (1971). *Acta Cryst.* B**27**, 11–23.

Di Blasio, B., Napolitano, G. & Pedone, C. (1977). *Acta Cryst.* B**33**, 542–545.

Dow, J., Jensen, L. H., Mazumdar, S. K., Srinivasan, R. & Ramachandran, G. N. (1970). *Acta Cryst.* B**26**, 1662–1671.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Jeffrey, G. A. & Saenger, W. (1991). In *Hydrogen Bonding in Biological Structures*. Berlin, Heidelberg, New York: Springer-Verlag.

Jiang, M., Xu, D. & Tan, Z. (1983). Abstracts of the VIIth International Conference on Crystal Growth, Stuttgart, Germany, p. 2.67.

Johnson, C. K. (1976). *ORTEP*II. Oak Ridge National Laboratory, Tennessee, USA.

Karle, I. L. & Karle, J. (1964). *Acta Cryst.* **17**, 835–841.

Koetzle, T. F., Golic, L., Lehmann, M. S., Verbist, J. J. & Hamilton, W. C. (1974). *J. Chem. Phys.* **60**, 4690–4696.

Monaco, S. B., Davis, L. E., Velsko, S. P., Wang, F. T., Eimerl, D. & Zalkin, A. (1987). *J. Cryst. Growth*, **85**, 252–255.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Pandiarajan, S., Sridhar, B. & Rajaram, R. K. (2001). *Acta Cryst.* E**57**, o466–o468.

Salunke, D. M. & Vijayan, M. (1981). *Int. J. Pept. Protein Res.* **18**, 348–351.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (1999). *PLATON for Windows*. Utrecht University, The Netherlands.

Sridhar, B., Srinivasan, N. & Rajaram, R. K. (2001). *Acta Cryst.* E**57**, o558--o560.

Srinivasan, N. & Rajaram, R. K. (1997). *Z. Kristallogr.* **212**, 311–312.

Srinivasan, N., Sridhar, B. & Rajaram, R. K. (2001). *Acta Cryst.* E**57**, o746–o748.

Zalkin, A., Eimeral, D. & Velsko, S. P. (1989). *Acta Cryst.* C**45**, 812–813.

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