

## L-Argininamidium bis(hydrogen-squarate)

Tsonko Kolev,<sup>a</sup> Michael Spitteller,<sup>b</sup> William S. Sheldrick<sup>c\*</sup> and Heike Mayer-Figge<sup>c</sup><sup>a</sup>Institute of Organic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. Build. 9, 1113 Sofia, Bulgaria, <sup>b</sup>Institut für Umweltforschung, Universität Dortmund, Otto-Hahn-Straße 6, 44221 Dortmund, Germany, and <sup>c</sup>Lehrstuhl für Analytische Chemie, Ruhr-Universität Bochum, Universitätsstraße 150, 44780 Bochum, Germany

Correspondence e-mail: william.sheldrick@rub.de

Received 9 February 2006

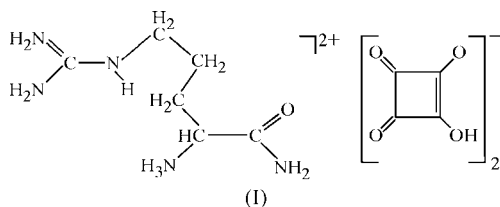
Accepted 3 April 2006

Online 22 April 2006

Cations and anions of the title compound [systematic name: 1-[4-(aminocarbonyl)butyl]guanidinium bis(hydrogen-squarate)],  $C_6H_{17}N_5O^{2+} \cdot 2C_4HO_4^-$ , are connected into a three-dimensional network by intermolecular N—H···O hydrogen bonds between the L-argininamidium ammonium, amide and guanidinium functions and the hydrogensquarate carbonyl O atoms. The independent hydrogensquarate monoanions are linked into dimers by pairs of O—H···O' hydrogen bonds.

## Comment

The search for new classes of organic compounds with second-order non-linear optical properties and high laser beam thresholds is directed towards crystalline materials with high dipole moments, asymmetrically conjugated  $\pi$ -electron systems and non-centrosymmetric crystal structures. Three main classes of organic compounds with different dimensionalities are known in the literature, *viz.* (a) one-dimensional compounds (dipoles), such as 4-nitroaniline and its derivatives, (b) two-dimensional compounds (quadrupoles), such as 4,6-dinitroresorcinole and its derivatives, and (c) three-dimensional compounds (octupoles), such as the guanidinium cation and its derivatives (Nalwa *et al.*, 1997; Wolff & Wortmann, 1999; Chemla & Zyss, 1987). In the course



of our spectroscopic and structural studies of optically active derivatives of amino acids, having non-linear optical and electro-optical properties, the crystal structure of the title compound, (I), has been determined. Structurally, (I) belongs to the C-amidated amino acids, whose salts and ester amides of

squaric acid represent a new class of compounds having great biological importance. We also publish the IR and Raman assignments of (I) for the first time. A structural study of some C-amidated amino acids, *viz.* Ile, Val, Thr, Ser, Met, Trp, Gln and Arg, was performed by In *et al.* (2001) and the results were compared to those for the C-unamidated counterparts.

The independent hydrogensquarate monoanions,  $HSq^-$ , are linked into dimers by  $O3'-H3' \cdots O8^{viii}$  and  $O7'-H7' \cdots O4^{ix}$  hydrogen bonds (Table 1). Such dimers have previously been reported for argininium hydrogensquarate (Angelova, Velikova *et al.*, 1996) and 4-phenylpyridinium hydrogensquarate (Kolev *et al.*, 2004), but infinite chains are also known, for instance in phenylglycine hydrogensquarate monohydrate (Angelova, Petrova *et al.*, 1996). In contrast to other amino acid amide derivatives, the L-argininamidium cations of (I) are not connected into helical chains by intermolecular N(amide)—H···O(amide) interactions (Kolev *et al.*, 2006). Translation-related cations of (I) are, however, linked by N(ammonium)—H···O(amide) hydrogen bonds (N2—

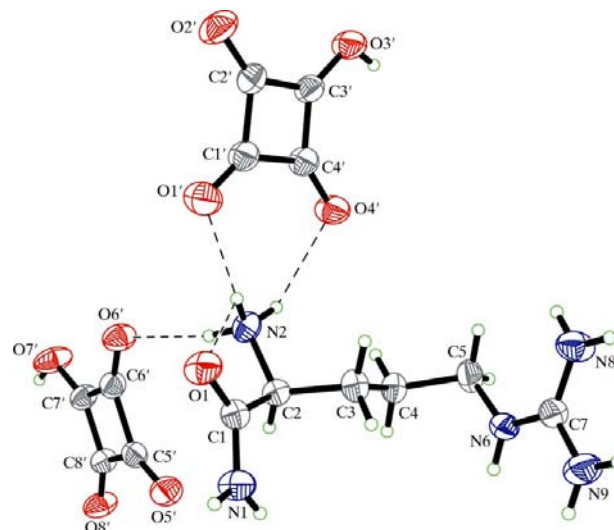


Figure 1

The molecular structure of (I), showing the atom-labelling scheme and the N2—H···O hydrogen bonds as dashed lines. Displacement ellipsoids are drawn at the 50% probability level.

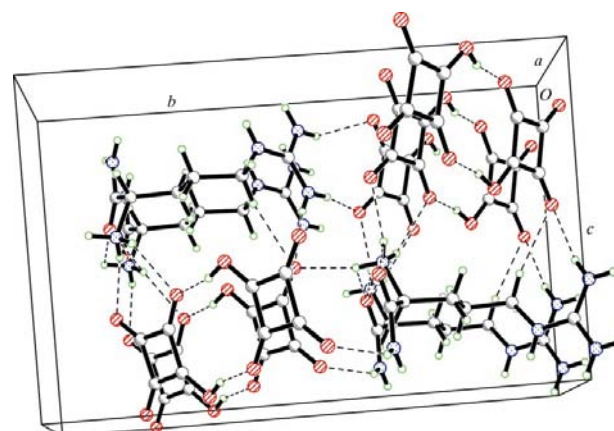


Figure 2

A projection of (I) perpendicular to [010], showing the three-dimensional network formed *via* intermolecular hydrogen bonds (dashed lines).

H22···O1<sup>iii</sup>; Table 1) into chains in the [100] direction. Additional intermolecular N—H···O hydrogen bonds to hydrogensquarate carbonyl O atoms, in which all possible donor NH atoms participate (Table 1), lead to the construction of a three-dimensional network.

### Experimental

The starting compound, L-argininamidium dihydrochloride, which is a white powder, was purchased from Bachem (Switzerland) and recrystallized from methanol. Compound (I) was synthesized by adding a methanol solution (10 ml) of L-argininamidium dihydrochloride (246 mg) to an aqueous solution (28 ml) of squaric acid (228 mg) and leaving the mixture to stand. Colourless crystals formed after four weeks and were filtered off and dried in air at room temperature. Single prismatic and colourless crystals suitable for X-ray analysis were grown from a methanol–water solution at room temperature over a period of two months. IR (KBr pellet, cm<sup>-1</sup>): 3426 (s), 3300 (m), 3200 (m) ν(NH<sub>2</sub>, guanidyl), 3338 ν<sub>as</sub>(NH, amino-carbonyl), 3151 ν<sub>s</sub>(NH, aminocarbonyl), 2865, 2790, 2740 ν(NH<sub>3</sub>, ammonium), 1804 (w) ν(CO, hydrogensquarate), 1689 (s) ν(C=O), 1655 (NH<sub>2</sub>, scissoring), 1619 (amide II), 1386 ν(CN, amide III), 1162, 1136 (w), 1109, 908 δ(NH<sub>2</sub>), 788 (amide VII), 722 (amide V). These data are in accordance with known values for other arginine-containing tri- and tetrapeptides (Kolev, 2006) obtained by IR–LD spectroscopy and theoretical (*ab initio* HF/6–31++G\*\*\*) calculations (Ivanova, 2005, 2006; Ivanova & Arnaudov, 2006). The results show a charge redistribution in the guanidyl fragment, leading to an observation of a broad IR absorption maximum in the whole 3400–2700 cm<sup>-1</sup> region assigned to stretching NH<sup>+</sup> and NH<sub>2</sub><sup>+</sup> vibrations.

#### Crystal data

C <sub>6</sub> H <sub>17</sub> N <sub>5</sub> O <sup>2+</sup> ·2C <sub>4</sub> HO <sub>4</sub> <sup>-</sup>	Z = 2
M <sub>r</sub> = 401.34	D <sub>x</sub> = 1.507 Mg m <sup>-3</sup>
Monoclinic, P2 <sub>1</sub>	Mo Kα radiation
a = 5.1850 (10) Å	μ = 0.13 mm <sup>-1</sup>
b = 16.668 (3) Å	T = 294 (2) K
c = 10.458 (2) Å	Prism, colourless
β = 101.90 (3)°	0.54 × 0.24 × 0.22 mm
V = 884.5 (3) Å <sup>3</sup>	

#### Data collection

Siemens P4 four-circle diffractometer	2659 independent reflections
ω scans	1972 reflections with I > 2σ(I)
Absorption correction: ψ scan (XPREP in SHELXTL-Plus; Sheldrick, 1995)	R <sub>int</sub> = 0.030
T <sub>min</sub> = 0.945, T <sub>max</sub> = 0.977	θ <sub>max</sub> = 30.0°
2919 measured reflections	3 standard reflections every 100 reflections intensity decay: 2%

#### Refinement

Refinement on F <sup>2</sup>	w = 1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> ) + (0.046P) <sup>2</sup> + 0.0784P]
R[F <sup>2</sup> > 2σ(F <sup>2</sup> )] = 0.045	where P = (F <sub>o</sub> <sup>2</sup> + 2F <sub>c</sub> <sup>2</sup> )/3
wR(F <sup>2</sup> ) = 0.099	(Δ/σ) <sub>max</sub> < 0.001
S = 1.01	Δρ <sub>max</sub> = 0.23 e Å <sup>-3</sup>
2659 reflections	Δρ <sub>min</sub> = -0.19 e Å <sup>-3</sup>
260 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.023 (4)

The S configuration of the argininamidium Cα atom C2 is known for the natural amino acid and was assigned to C2. As atoms heavier than Si are not present in (I), anomalous scattering contributions are negligible and no Friedel pairs were measured. H atoms were treated as riding, with C—H = 0.97 Å for the methylene C atoms and 0.98 Å for atom C2, N—H = 0.89 Å for ammonium atom N2 and 0.86 Å for

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H11···O5 <sup>ri</sup>	0.86	2.37	3.095 (3)	143
N1—H12···O2 <sup>iii</sup>	0.86	2.15	2.986 (3)	165
N2—H23···O1	0.89	2.24	2.646 (3)	107
N2—H22···O1 <sup>iii</sup>	0.89	2.52	2.831 (3)	101
N2—H23···O1 <sup>i</sup>	0.89	2.06	2.836 (3)	145
N2—H22···O4 <sup>i</sup>	0.89	2.27	3.007 (3)	140
N2—H21···O6 <sup>i</sup>	0.89	1.97	2.841 (3)	166
N6—H6···O8 <sup>iv</sup>	0.86	2.27	3.054 (3)	151
N8—H82···O1 <sup>rv</sup>	0.86	1.99	2.842 (3)	168
N8—H81···O6 <sup>vi</sup>	0.86	2.03	2.863 (3)	162
N9—H91···O2 <sup>rv</sup>	0.86	2.29	3.066 (4)	150
N9—H92···O5 <sup>vii</sup>	0.86	2.51	2.898 (3)	108
N9—H92···O8 <sup>iv</sup>	0.86	2.27	3.035 (4)	149
O3 <sup>i</sup> —H3 <sup>i</sup> ···O8 <sup>viii</sup>	0.82	1.74	2.523 (3)	160
O7 <sup>i</sup> —H7 <sup>i</sup> ···O4 <sup>ix</sup>	0.82	1.79	2.564 (3)	158

Symmetry codes: (i) x + 1, y, z; (ii) x, y, z + 1; (iii) x - 1, y, z; (iv) -x + 1, y - ½, -z + 2; (v) -x + 2, y - ½, -z + 1; (vi) -x + 1, y - ½, -z + 1; (vii) -x + 2, y - ½, -z + 2; (viii) -x, y - ½, -z + 1; (ix) -x, y + ½, -z + 1.

all other N atoms, and O—H = 0.82 Å [U<sub>iso</sub>(H) = 1.2U<sub>eq</sub>(C2,C5), 1.35U<sub>eq</sub>(N2), 1.2U<sub>eq</sub>(N6,N8,N9), 1.2U<sub>eq</sub>(O7<sup>i</sup>); all other U<sub>iso</sub>(H) values were refined freely].

Data collection: R3m/V (Siemens, 1989); cell refinement: R3m/V; data reduction: XDISK (Siemens, 1989); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL-Plus (Sheldrick, 1995).

TK and MS thank the DAAD for a grant within the priority programme ‘Stability Pact South-Eastern Europe’, the Alexander von Humboldt Foundation and the Bulgarian National Fund for Research (grant No. X-1213).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KP2003). Services for accessing these data are described at the back of the journal.

### References

- Angelova, O., Petrova, R., Radomirska, V. & Kolev, T. (1996). *Acta Cryst.* **C52**, 2218–2220.
- Angelova, O., Velikova, V., Radomirska, V. & Kolev, T. (1996). *Acta Cryst.* **C52**, 3252–3256.
- Chemla, D. S. & Zyss, J. (1987). Editors. *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. 1, pp. 23–187. New York: Academic Press.
- In, Y., Fujii, M., Sasada, Y. & Ishida, T. (2001). *Acta Cryst.* **B57**, 72–81.
- Ivanova, B. B. (2005). *Spectrochim. Acta Part A*, **62**, 58–62.
- Ivanova, B. B. (2006). *J. Mol. Struct.* **782**, 122–129.
- Ivanova, B. B. & Arnaudov, M. G. (2006). *Spectrochim. Acta Part A*. In the press.
- Kolev, T. (2006). *Biopolymers*. Submitted.
- Kolev, T., Wortmann, R., Spittler, M., Sheldrick, W. S. & Heller, M. (2004). *Acta Cryst.* **E60**, o956–o957.
- Kolev, T., Yancheva, D., Spittler, M., Sheldrick, W. S. & Mayer-Figge, H. (2006). *Acta Cryst.* **E62**, o463–o465.
- Nalwa, H. S., Watanabe, T. & Miyata, S. (1997). *Nonlinear Optics of Organic Molecules and Polymers*, edited by H. S. Nalwa & S. Miyata, pp. 89–329. Boca Raton: CRC Press Inc.
- Sheldrick, G. M. (1995). *SHELXTL-Plus*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1989). *R3m/V* (Version 3.2) and *XDISK*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Wolff, J. J. & Wortmann, R. (1999). *Adv. Phys. Org. Chem.* **32**, 121–217.