The structure was solved manually by the Patterson method. The initial refinement in the noncentrosymmetric $Pn2_1a$ (No. 33) space group converged to $R = 0.024$ and $wR = 0.039$, but gave unsatisfactory molecular geometry in the choline part of the cation. The structure was then refined in the centrosymmetric $Pnma$ (No. 62) space group, with positioning of the ions on a mirror plane and allowing one methylene C atom to be statistically disordered on both sides of the plane. The positions of all H atoms, except the methyl H atoms, were calculated and included in the refinement with a riding geometry. Methyl H atoms were found in difference Fourier maps and their positions were normalized and included in the refinement as riding.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *Structure Determination Package* (Enraf–Nonius, 1985). Program(s) used to refine structure: *Structure Determination Package*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *KAPPA* (Macíček, 1992).

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# Crystalline Complexes Involving Amino Acids. II. (R)-(−)-1-Phenylglycinium Hydrogen Squarate Monohydrate

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## Abstract

The title compound, $C_8H_{10}NO_2^+.C_4HO_4^-.H_2O$, crystallizes in the orthorhombic space group $P2_12_12_1$ in a layered structure of charged phenylglycinium and squarate/water layers stacked along the $c$ axis and held together by an extensive hydrogen-bonding network. The amino group of the phenylglycine molecule adopts a proton from the squaric acid. The C—C bond lengths within the squarate anion are consistent with a delocalized double bond around the hydroxyl-bearing C atom: 1.414 (3) and 1.431 (3) Å *versus* 1.481 (3) and 1.494 (3) Å for the opposite bonds in the ring.

## Comment

The structure determination reported here was undertaken as part of a project investigating the non-linear optical properties of new classes of organic compounds involving salts of optically active amino acids, amines and guanidine derivatives with 'oxocarbons' (West, 1980) – deltic, squaric, croconic and rhodisonic acids as well as its sulfur derivatives. The series has been started with the structure of the L-argininium hydrogen squarate (Angelova, Velikova, Radomirska & Kolev, 1996).

The title structure (I) is built up from layers of phenylglycinium cations and squarate anions stacked along the $c$ axis. The phenyl and squarate rings are almost coplanar, the dihedral angle between them being 5.7 (3)°. The closest distance between their planes is 3.305 (2) Å.



(I)
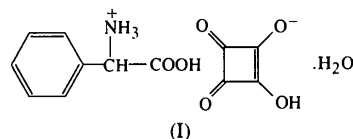
The $\alpha$-amino group in phenylglycine is protonated and the corresponding C2—N bond length is 1.503 (3) Å, similar to those found in the crown ether inclusion complexes with phenylglycine methyl (Goldberg, 1977; Courtois, Masdouri, Genin & Gross, 1986)

and ethyl ester (Alberts, Timmer, Noltes & Spek, 1979) and insignificantly shorter than the bond lengths in the neutral ($DL$-phenylglycine)$_4$Mo$_2$L$_4$.6H$_2$O complex [1.52 (1) Å; Apfelbaum-Tibika & Bino, 1984]. The small dihedral angle of 11.2 (8)° between the N—C2—C1 and C1—O1—O2 planes is consistent with an intramolecular hydrogen bond of the type O1···HN1—N with an O1···HN1 distance of 2.23 (1) and O1···N of 2.633 (3) Å. The corresponding N—HN1···O1 angle is 103.8 (1)°. The phenyl ring is rotated by 90.3 (1)° with respect to the N—C2—C1 plane.
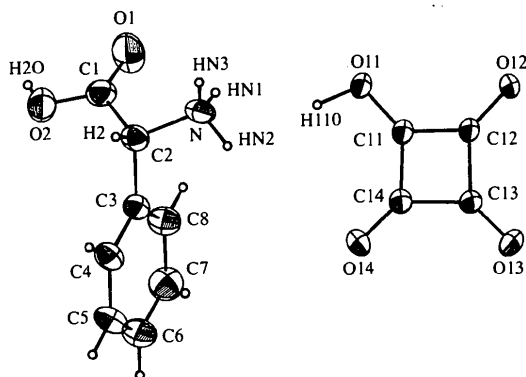


Fig. 1. The ions with the atom-numbering scheme; 30% probability displacement ellipsoids are shown. H atoms are drawn as circles of arbitrary radius.
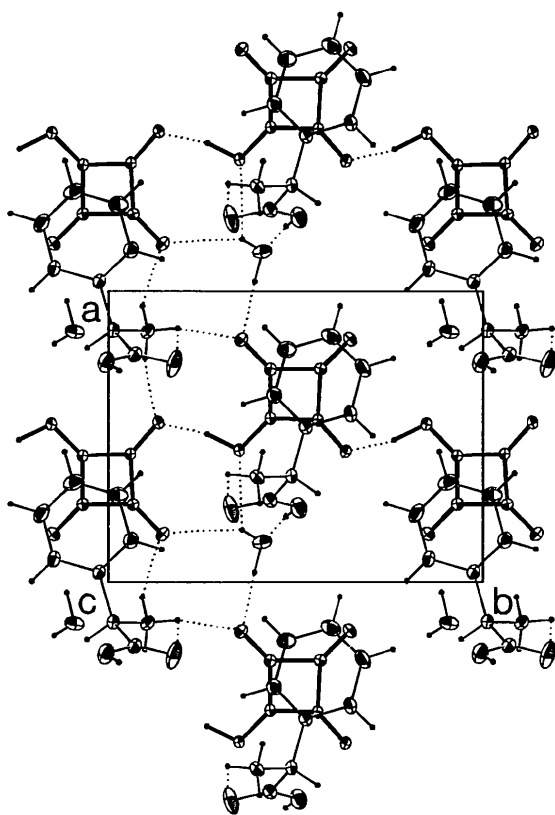


Fig. 2. Projection of the structure down the $c$ axis. Dotted lines denote hydrogen bonds.

The bond lengths and angles within the squaric acid ring correspond to a delocalized three-centred double C—C bond around C11 [C11—C12 1.414 (3) and C11—C14 1.431 (3) Å] and mainly single bonds around C13 [C13—C12 1.481 (3) and C13—C14 1.494 (3) Å]. The same bond-length distribution occurs in the $L$-argininium hydrogen squarate (Angelova *et al.*, 1996) and in the cobalt and nickel squarate octahydrate (Brach, Rozière, Anselment & Peters, 1987). The squarate ring is bent by 3.5 (8)° along the C12···C14 direction.

The structural units are held together by an extensive hydrogen-bonding network (see Table 3). The squarate anions form strongly hydrogen-bonded chains along the $b$ axis. The H atoms of the water molecule are placed in positions to interlink the squarate anions while its O atom is accepting the carboxyl and amino H atoms from phenylglycinium cations in two adjacent layers. Interestingly, the water molecule takes part in one short (HW1···O14) and one longer bifurcated [HW2···O11 ($x-1$, $y$, $z$), HW2···O13($-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$)] hydrogen-donating bond and one short OW···H2O($-\frac{1}{2}-x$, $-y$, $\frac{1}{2}+z$) and one long (OW···HN2) hydrogen-accepting bond.

## Experimental

The title compound has been prepared by adding an aqueous solution of phenylglycine free base to a solution of squaric acid in 1:1 molar ratio. The product has been purified by multifold recrystallization from bidistilled water. Colourless crystals suitable for X-ray analysis were grown by slow evaporation from an aqueous solution at room temperature.

### Crystal data

| | |
|---|---|
| $C_8H_{10}NO_2^+.C_4HO_4^-.H_2O$ | Mo $K\alpha$ radiation |
| $M_r = 283.23$ | $\lambda = 0.71073$ Å |
| Orthorhombic | Cell parameters from 22 |
| $P2_12_12_1$ | reflections |
| $a = 8.366 (2)$ Å | $\theta = 20.21–21.12°$ |
| $b = 11.066 (2)$ Å | $\mu = 0.10$ mm$^{-1}$ |
| $c = 14.562 (2)$ Å | $T = 292$ K |
| $V = 1348.1 (8)$ Å$^3$ | Prismatic |
| $Z = 4$ | $0.52 \times 0.52 \times 0.39$ mm |
| $D_x = 1.395$ Mg m$^{-3}$ | Colourless |
| $D_m$ not measured | |

### Data collection

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | 2293 observed reflections [$I > 3.0\sigma(I)$] |
| Continuous profile scans | $R_{int} = 0.014$ |
| Absorption correction: | $\theta_{max} = 28.0°$ |
| empirical based on $\psi$ | $h = 0 \rightarrow 11$ |
| scans (North, Phillips & Mathews, 1968) | $k = 0 \rightarrow 14$ |
| $T_{min} = 0.955$, $T_{max} = 0.997$ | $l = -19 \rightarrow 19$ |
| | 3 standard reflections |
| | frequency: 120 min |
| 3650 measured reflections | intensity decay: none |
| 3251 independent reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F$ | $w = 1/[\sigma^2(F) + (0.020F)^2]$ |
| $R = 0.045$ | $(\Delta/\sigma)_{max} = 0.023$ |
| $wR = 0.057$ | $\Delta\rho_{max} = 0.288$ e Å$^{-3}$ |
| $S = 1.112$ | $\Delta\rho_{min} = -0.348$ e Å$^{-3}$ |
| 2293 reflections | Extinction correction: none |
| 193 parameters | Atomic scattering factors |
| All H-atom parameters | from *SDP/PDP* (Enraf– |
| refined | Nonius, 1985) |

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| O11 | 0.5447 (2) | −0.1522 (1) | 0.2580 (2) | 0.0633 (5) |
| O12 | 0.5499 (2) | 0.1326 (1) | 0.2393 (1) | 0.0559 (5) |
| O13 | 0.1654 (2) | 0.1440 (1) | 0.2721 (1) | 0.0463 (4) |
| O14 | 0.1668 (2) | −0.1470 (1) | 0.3081 (1) | 0.0466 (4) |
| O1 | −0.2485 (3) | 0.1741 (2) | 0.0124 (1) | 0.0925 (7) |
| O2 | −0.2441 (2) | −0.0069 (2) | −0.0504 (1) | 0.0698 (5) |
| N | −0.1386 (2) | 0.1039 (2) | 0.1731 (1) | 0.0438 (4) |
| OW | −0.1394 (2) | −0.0906 (2) | 0.3052 (1) | 0.0562 (4) |
| C11 | 0.4356 (2) | −0.0692 (2) | 0.2685 (2) | 0.0400 (5) |
| C12 | 0.4416 (2) | 0.0578 (2) | 0.2582 (2) | 0.0386 (5) |
| C13 | 0.2672 (2) | 0.0646 (2) | 0.2745 (1) | 0.0337 (4) |
| C14 | 0.2683 (2) | −0.0690 (2) | 0.2890 (1) | 0.0345 (4) |
| C1 | −0.2174 (3) | 0.0696 (2) | 0.0148 (2) | 0.0487 (6) |
| C2 | −0.1345 (2) | 0.0123 (2) | 0.0969 (2) | 0.0410 (5) |
| C3 | 0.0347 (2) | −0.0253 (2) | 0.0742 (1) | 0.0378 (5) |
| C4 | 0.0795 (3) | −0.1453 (2) | 0.0829 (2) | 0.0489 (6) |
| C5 | 0.2369 (3) | −0.1783 (2) | 0.0610 (2) | 0.0634 (7) |
| C6 | 0.3439 (3) | −0.0934 (3) | 0.0325 (2) | 0.0665 (7) |
| C7 | 0.2998 (3) | 0.0257 (3) | 0.0237 (2) | 0.0596 (7) |
| C8 | 0.1444 (3) | 0.0590 (2) | 0.0442 (2) | 0.0500 (6) |

Table 2. *Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O11—C11 | 1.304 (2) | C13—C14 | 1.494 (3) |
| O12—C12 | 1.257 (2) | C1—C2 | 1.521 (3) |
| O13—C13 | 1.223 (2) | C2—C3 | 1.512 (3) |
| O14—C14 | 1.242 (2) | C3—C4 | 1.385 (3) |
| O1—C1 | 1.186 (3) | C3—C8 | 1.380 (3) |
| O2—C1 | 1.292 (3) | C4—C5 | 1.403 (4) |
| N—C2 | 1.503 (3) | C5—C6 | 1.362 (4) |
| C11—C12 | 1.414 (3) | C6—C7 | 1.374 (4) |
| C11—C14 | 1.431 (3) | C7—C8 | 1.385 (4) |
| C12—C13 | 1.481 (3) | | |
| | | | |
| O11—C11—C12 | 131.5 (2) | O14—C14—C11 | 135.6 (2) |
| O11—C11—C14 | 135.2 (2) | O14—C14—C13 | 135.6 (2) |
| C12—C11—C14 | 93.2 (2) | C11—C14—C13 | 88.7 (1) |
| O12—C12—C11 | 134.7 (2) | O1—C1—O2 | 125.4 (3) |
| O12—C12—C13 | 135.4 (2) | O1—C1—C2 | 122.0 (2) |
| C11—C12—C13 | 89.9 (2) | O2—C1—C2 | 112.5 (2) |
| O13—C13—C12 | 135.9 (2) | N—C2—C1 | 106.8 (2) |
| O13—C13—C14 | 135.9 (2) | N—C2—C3 | 111.6 (2) |
| C12—C13—C14 | 88.1 (1) | C1—C2—C3 | 111.7 (2) |

Table 3. *Hydrogen-bonding geometry*

| D—H···A | D—H | H···A | D···A | D—H···A | A¹···H···A² |
|---|---|---|---|---|---|
| O11—H11O···O12$^i$ | 1.05 (1) | 1.48 (1) | 2.509 (2) | 166 (1) | |
| OW—HW1···O14 | 0.91 (1) | 1.73 (1) | 2.637 (2) | 177 (1) | |
| OW—HW2···O11$^{ii}$ | 0.71 (1) | 2.35 (1) | 2.815 (2) | 124 (1) | 86 (1) |
| OW—HW2···O13$^{iii}$ | 0.71 (1) | 2.53 (1) | 3.153 (2) | 147 (1) | |
| O2—H2O···OW$^{iv}$ | 0.77 (2) | 1.79 (1) | 2.557 (3) | 172 (1) | |
| N—HN1···O14$^v$ | 0.94 (2) | 2.00 (1) | 2.781 (2) | 138 (1) | 104 (1) |
| N—HN1···O1 | 0.94 (2) | 2.23 (1) | 2.633 (3) | 104 (1) | |
| N—HN2···O3 | 0.95 (2) | 2.09 (1) | 2.957 (2) | 150 (1) | 105 (1) |
| N—HN2···OW | 0.95 (2) | 2.51 (1) | 2.886 (3) | 104 (1) | |
| N—HN3···O12$^{ii}$ | 0.88 (2) | 1.96 (1) | 2.797 (2) | 159 (1) | |

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

The complex has been characterized by elemental analysis and spectroscopic methods. Its specific optical rotation, $[\alpha]_D^{20} = 21.26°$, was measured in water solution. The solid-state (KBr pellet) IR spectrum confirms that the carboxyl group is deprotonated, $\nu_{C=O}$ is at 1715 cm$^{-1}$, and the amino group is protonated. The strong peaks at 3480 and 3190 cm$^{-1}$ and the other bands at *ca* 3000 cm$^{-1}$ show the existence of a network of strong hydrogen bonds. The melting point of phenyl-glycinium hydrogen squarate monohydrate is over 580 K with decomposition. All H atoms have been localized from difference Fourier maps and refined with fixed displacement parameters, $U_{iso} = 0.063$ Å$^2$.

Data collection: *CAD*-4 (Enraf–Nonius, 1988). Data reduction: *SDP/PDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SDP/PDP*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, 1992).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1238). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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