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L-Tyrosinamide hydrochloride monohydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.029
wR factor = 0.079
Data-to-parameter ratio = 14.6

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

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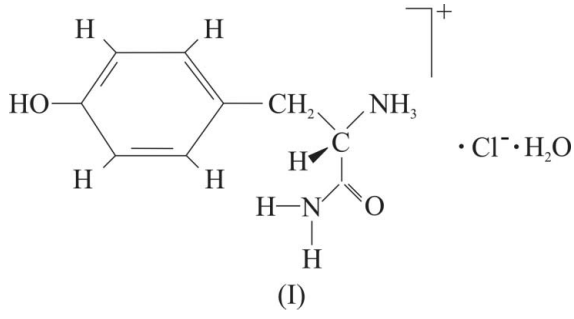
Cations of the title compound, 1-carbamoyl-2-(4-hydroxyphenyl)ethylammonium chloride monohydrate, $C_9H_{13}N_2O_2^+\cdot Cl^-\cdot H_2O$, are connected by intermolecular N—H···O [N···O = 2.905 (3) Å] hydrogen bonds between the amide and 4-hydroxy functions into helical chains propagating along the [010] axis. The Cl^- ions and water O atom participate in a complex pattern of hydrogen bonds to link these ribbons into a three-dimensional network.

Comment

In the course of our spectroscopic and structural studies of some optically active derivatives of amino acids having nonlinear optical and electro-optical properties (Nalwa *et al.*, 1997; Wolff & Wortmann, 1999; Chemla & Zyss, 1987), the crystal structure of the title compound, (I), has been determined.



(I)

The salts of C-amidated amino acids and ester amides of squaric acid represent a new class of compounds of considerable biological importance. A structural study of the C-amidated amino acids of Ile, Val, Thr, Ser, Met, Trp, Gln and Arg has been performed and the results compared with the free acids (In *et al.*, 2001). It is known that most mammalian peptide hormones possess a C-terminal α-amide, as exemplified by calcitonin, gastrin, neurokinins, neuropeptides and their related peptides (Eipper & Mains, 1988). In many cases, C-amides are much more biologically active than the corresponding C-terminal free acids. The importance of the C-terminal amide for bioactivity can be illustrated by the 'potency ratio', which is defined as the relative potency of a peptide amide divided by the relative potency of the corresponding peptide free acid. For instance, neurocinin A possesses a potency ratio greater than 10^4 (Merkler 1994; Suwan *et al.*, 1994). At present, the biological–structural function of the C-amide is still not fully understood. The amidation arises from the oxidative cleavage of C-terminal glycine-extended prohormones (Kulathila *et al.*, 1999). Since

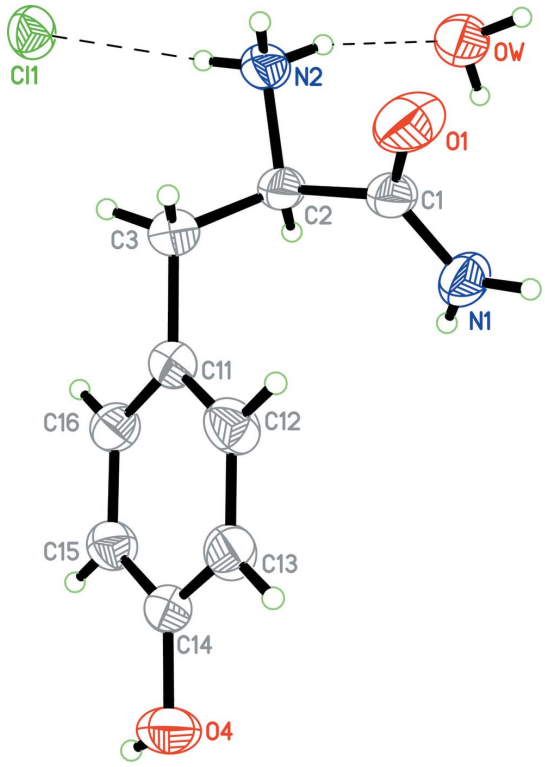


Figure 1
A view of (I), with hydrogen bonds to the Cl^- ion and the water molecule shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level.

Cl^- anions are present in living cells, the present structural information may be useful in understanding the different biological roles of C-amide and C-acid peptides.

The IR spectrum of (I) (KBr pellet) exhibits characteristic sharp ν(OH) bands for OH functions connected *via* hydrogen bonds. A band of medium intensity appears at 3380 cm^{-1}, which can be assigned to ν(OH) of the water molecule, and the neighbouring band at 3334 cm^{-1} can be attributed to the similar vibration of the tyrosine OH group. The bands at 3276 and 3210 cm^{-1} could possibly be assigned to ν(NH) of the ammonium group, but the bands belonging to ν(NH) of the amide group are also expected in the same region. The presence of strong overlapping for these absorption peaks in tyrosine-containing peptides makes a detailed assignment difficult, but it is reasonable to assign the observed bands to the latter function (Ivanova, 2005*a*,*b*). In the Raman spectrum of (I), only two sharp bands at 3335 and 3276 cm^{-1} of medium intensity appear. These are accordingly attributed to ν(OH) of the phenol group and the symmetric ν(NH) of the amide group.

The very intense and highly symmetric ν(C=O) (amide I) band of (I) is observed at 1646 cm^{-1} (IR) but is very weak in the Raman spectrum. The band belonging to the asymmetric scissoring vibration of the NH_3 group is found at 1621 cm^{-1} (IR) and 1620 cm^{-1} (Raman). A band at 1594 cm^{-1} appears as a shoulder to the strong band at 1646 cm^{-1} and is assigned to the aromatic ring radial vibration 8*a*. The band at 1446 cm^{-1} belongs to the 19*b* mode of the aromatic ring and exhibits intermediate intensity. Other prominent bands are those at 1517 and 1471 cm^{-1} (IR) belonging to, respectively, the second asymmetric and symmetric deformation vibrations of the NH_3 group. In the Raman spectrum, the corresponding bands are very weak and have no diagnostic value. The C—N stretching vibration and NH_3 rocking modes in this class can couple. Nevertheless, the stretching C—N vibration is unambiguously assigned to the band at 1014 cm^{-1} in the IR and 1015 cm^{-1} in the Raman spectrum. For the NH_3 rocking mode, three bands at, respectively, 1175, 1106 and 936 cm^{-1} can be taken into account. The strong band at 1255 cm^{-1} could be assigned to the ν(C—O) vibration of the hydroxyl group but this assignment must be regarded as tentative.

The vibrational spectra of (I) can be compared with those of a series of salts of natural amino acid amides and the expected ranges of different characteristic vibrations with analytical value can be established. Detailed vibrational and quantum-chemical investigations are in progress and will be published at a later date.

The asymmetric unit of (I) is shown in Fig. 1, with a view along the [010] axis being depicted in Fig. 2.

Cations of (I) are linked through N1—H11$\cdots$O4^{ii} hydrogen bonds (Table 1) into helical chains in the [010] direction. The Cl^- ions function as hydrogen-bond acceptors in interactions with the ammonium atom N2, leading to sheets perpendicular to the [001] axis. They also participate in hydrogen bonds to the water atom O*W*, which in turn is an acceptor in the interactions with the ammonium group N2 (Table 1). These contacts lead to the formation of a three-dimensional network.

Experimental

Compound (I) was received as a white powder from Bachem (Switzerland) and recrystallized four times, first from water–ethanol (1:1 *v*/*v*) and then three times from 96% ethanol. The IR and Raman spectra of (I) were measured after each recrystallization and confirmed the compound stability. Single prismatic colourless crystals, suitable for X-ray analysis, were grown from methanol at room temperature over a period of a week.

Crystal data

$C_9H_{13}N_2O_2^+\cdot Cl^-\cdot H_2O$
M_r = 234.68
Monoclinic, $P2_1$
a = 7.3671 (17) Å
b = 6.020 (2) Å
c = 13.689 (3) Å
β = 105.551 (12)°
V = 584.9 (3) Å^3
Z = 2
D_x = 1.332 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 reflections
θ = 7.5–12.5°
μ = 0.32 mm^{-1}
T = 293 (2) K
Block, colourless
0.59 × 0.46 × 0.43 mm

Data collection

Siemens P4 four-circle diffractometer
Profile-fitted ω scans
Absorption correction: ψ scan (*SHELXTL-Plus*; Sheldrick, 1998)
T_{min} = 0.790, T_{max} = 0.875
2595 measured reflections
2136 independent reflections
1966 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 30.0°
$h = -1 \rightarrow 10$
$k = -8 \rightarrow 8$
$l = -19 \rightarrow 18$
3 standard reflections
every 100 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.079$
$S = 1.04$
2136 reflections
146 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 0.0448P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.150 (11)
Absolute structure: Flack (1983), with 293 Friedel pairs
Flack parameter: −0.04 (6)

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···Cl1^{i}	0.82	2.37	3.0576 (16)	142
N1—H11···O4^{ii}	0.86	2.06	2.905 (3)	167
N2—H22···Cl1	0.89	2.34	3.2206 (17)	170
N2—H21···*OW*	0.89	2.02	2.884 (2)	164
N2—H23···*OW*^{iii}	0.89	2.00	2.890 (3)	173
OW—*HW*1···Cl1^{iii}	0.83 (1)	2.35 (1)	3.1601 (17)	164 (3)
OW—*HW*2···Cl1^{iv}	0.83 (1)	2.43 (1)	3.2523 (16)	171 (3)

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

The water H atoms were located in difference syntheses and refined freely with isotropic displacement parameters under the restraint *OW*—H = 0.83 (1) Å. The H atoms of the cation were constrained to idealized positions and refined using a riding model, with C—H = 0.93 Å for aromatic H, 0.97 Å for methylene atoms H31 and H32 and 0.98 Å for C2—H2, N—H = 0.86 Å for amide H and 0.89 Å for ammonium H, and O4—H4 = 0.82 Å for the hydroxyl group. U_{iso}(H) = 1.2U_{eq}(C,N), or 1.5U_{eq}(O4) in the case of H4. The *S* configuration of the tyrosine α-C atom C2 is known for the natural amino acid and was confirmed by refinement of the Flack parameter (Flack, 1983) to −0.04 (6), based on 293 measured Friedel pairs.

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, 1998); software used to prepare material for publication: *SHELXL97*.

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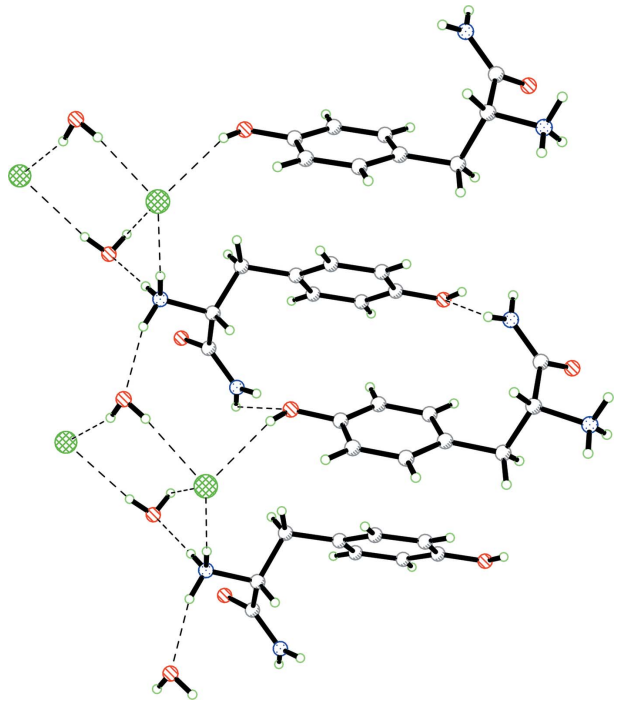

Figure 2
The hydrogen-bonding pattern (dashed lines) linking helical chains of the cation of (I) into a three-dimensional network.

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