ORGANIC COMPOUNDS

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L-Histidylglycinium Chloride, $C_8H_{13}N_4O_3^+.Cl^-$

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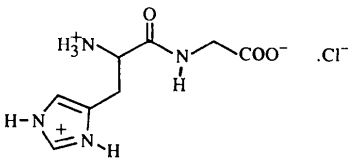
Abstract

The title peptide crystallized as a monocation with a protonated histidine side chain. The molecules form dimers connected by a tight system of hydrogen bonds, which includes an unusually short Cα—H···O interaction with a C···O separation of 3.030 (3) Å.

Comment

The crystal structure of the dipeptide salt L-His-Gly chloride, (1), was determined in order to characterize the hydrogen-bond interactions. As expected, the dipeptide carries positive charges at the N1 atom and at the imidazole ring, whereas the acid group is deprotonated [Fig. 1(*a*)]. In the crystal lattice, peptide molecules form dimers which are connected by a tight system of hydrogen bonds (Fig. 2). It is worthwhile pointing out the short C1—H···O2 contact; amino acid Cα—H is known to be quite a strong C—H···O hydrogen-bond donor (Jeffrey & Maluszynska, 1982; Steiner, 1995; Derewenda, Lee & Derewenda, 1995), but an intermolecular C···O distance of only 3.030 (3) Å is exceptional. More typical are Cα···O separations > 3.2 Å. Note how the O2 atom is chelated by the parallel hydrogen-bond donors N2—H and Cα—H.



(1)

In Fig. 1(*b*), the molecular structure in the L-His-Gly dichloride salt, (2) (Steiner, 1997), is shown for comparison. There are two major conformational differences: in the peptide backbone, the C2—N2—C3—C4 torsion angle, Φ, is 175.1 (3)° in (1) and 67.5 (4)° in (2), and in the His side chain, the imidazole ring is rotated by 176° [torsion angle C1—C5—C6—C7 is 96.3 (4)° in (1) and −87.7 (5)° in (2)]. It is of interest that in (1) and (2), the His residues form contacts to Cl^- which are topologically analogous (Fig. 1). Because of the 176° rotation of the imidazole ring, C7—H and N3—H have changed roles, so that the N3—H···Cl^- hydrogen bond in (2) (H···Cl 2.56 Å) is replaced by a C7—H···Cl^- contact

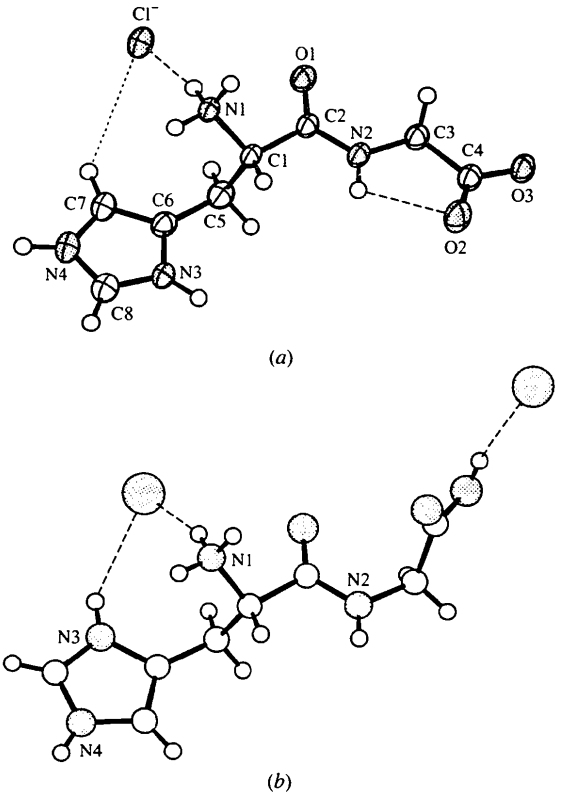


Fig. 1. (*a*) The molecular structure and atom labelling of the title compound. Displacement ellipsoids are drawn at the 50% probability level. (*b*) The molecular structure in L-His-Gly dichloride (Steiner, 1997). The dipeptides are drawn in the same projection with respect to the peptide bonds. O and N atoms and Cl^- ions are drawn shaded.

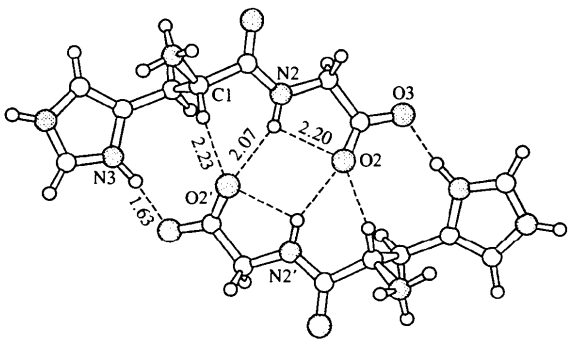


Fig. 2. Arrangement of the molecular dimer. H···*X* distances are given for normalized H-atom positions. Note that the Cα—H···O contact is associated with a Cα···O separation of only 3.030 (3) Å.

in (1). Due to the very long H7···Cl^- distance (3.14 Å), this contact would normally remain unattended, but the obvious similarity of the patterns can suggest some (certainly minor) stabilizing function.

Experimental

L-His-Gly is commercially available (Sigma). Recrystallization by slow evaporation of a solution in 6% HCl yielded the crystalline dichloride salt (L-His-Gly)$^{2+}$.2Cl^-. An equimolar mixture of L-His-Gly and L-His-Gly dichloride was dissolved in water and crystals of (L-His-Gly)$^+$.Cl^- were obtained by slow evaporation.

Crystal data

$C_8H_{13}N_4O_3^+.Cl^-$
M_r = 248.67
Monoclinic
$C2$
a = 16.698 (2) Å
b = 7.0361 (5) Å
c = 9.7093 (13) Å
β = 108.754 (11)°
V = 1080.2 (2) Å^3
Z = 4
D_x = 1.529 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54176 Å
Cell parameters from 25 reflections
θ = 11.2–25.9°
μ = 3.174 mm^{-1}
T = 293 (2) K
Plate
0.35 × 0.25 × 0.05 mm
Colourless

Data collection

Enraf–Nonius Turbo-CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.687, T_{max} = 0.853
2229 measured reflections
1159 independent reflections

1116 reflections with $I > 2\sigma(I)$
R_{int} = 0.0279
θ_{max} = 59.82°
$h = -18 \rightarrow 18$
$k = -7 \rightarrow 2$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 30 min
intensity decay: 2.2%

Refinement

Refinement on F^2
$R(F)$ = 0.0318
$wR(F^2)$ = 0.0864
S = 1.072
1159 reflections
160 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2 + 0.195P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.221 e Å^{-3}
$\Delta\rho_{min}$ = −0.266 e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0009 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.00 (2)

Table 1. *Selected geometric parameters (Å, °)*

O2—C4	1.232 (3)	N4—C8	1.323 (4)
O3—C4	1.265 (4)	N4—C7	1.372 (4)
N3—C8	1.317 (4)	C6—C7	1.358 (4)
N3—C6	1.384 (4)		
C2—N2—C3	123.0 (2)		
C3—N2—C2—O1	−3.9 (7)	N2—C3—C4—O2	−4.5 (5)
C3—N2—C2—C1	173.9 (3)	N2—C3—C4—O3	176.6 (3)
C5—C1—C2—O1	86.2 (4)	N1—C1—C5—C6	−58.1 (3)
N1—C1—C2—N2	146.4 (3)	C2—C1—C5—C6	−178.3 (2)
C5—C1—C2—N2	−91.6 (4)	C1—C5—C6—C7	96.3 (4)
C2—N2—C3—C4	175.1 (3)	C1—C5—C6—N3	−79.3 (4)

Table 2. *Selected hydrogen-bond parameters (Å, °)*

Data for normalized H-atom positions are based on bond lengths of O—H = 0.98, N—H = 1.04 and C—H = 1.09 Å.

	H···A	D···A	D—H···A
N1—H1N1···Cl^{i}	2.17	3.141 (3)	154
N1—H1N1···O1^{i}	2.53	2.893 (4)	100
N1—H2N1···O3^{ii}	1.83	2.795 (3)	153
N1—H3N1···Cl	2.21	3.240 (2)	171
N2—HN2···O2^{iii}	2.07	3.012 (3)	150
N2—HN2···O2	2.20	2.627 (3)	102
N3—HN3···O3^{iii}	1.63	2.650 (3)	167
N3—HN3···O2^{iii}	2.56	3.350 (3)	133
N4—HN4···Cl^{iv}	2.11	3.041 (3)	147
C1—H1···O2^{iii}	2.23	3.030 (3)	129
C5—H15···O1^{v}	2.66	3.620 (4)	147
C5—H25···O2^{iii}	2.73	3.250 (4)	109
C7—H7···Cl	3.14	3.985 (3)	135
C8—H8···Cl^{vi}	2.58	3.654 (3)	168

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

X-ray diffraction data were measured on a specimen glued to a glass pin. After anisotropic refinement of the non-H atoms, all H atoms were unambiguously located in difference Fourier calculations. The H atoms were then treated in the default riding model of *SHELXL*93 (Sheldrick, 1993), with the NH_3^+ group allowed to rotate and U_{eq} allowed to vary. Since the U_{eq} parameters of all H atoms refined to realistic values < 0.1 Å^2, this treatment can be regarded as reasonable. For calculation of the geometric hydrogen-bond parameters (Table 3), the H atoms of the final model were shifted along the X—H bonds to average neutron-determined $d(X$—H) values ('normalization').

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*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

The author thanks Professor W. Saenger for giving him the opportunity to carry out this study in his laboratory.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: SX1019). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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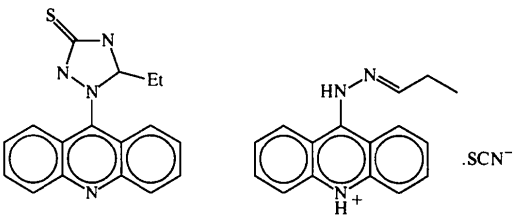

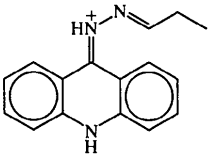

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9-Propylidenehydrazino-10-acridinium Thiocyanate at 173 K

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Abstract

The acridinium ring in the title compound, $C_{16}H_{16}N_3^+.SCN^-$, deviates slightly from planarity; the angle between the planes of the outer rings is 6.20 (14)°. There are significant distortions of the hydrazine side chain caused by steric interactions with the acridinium ring. The cations stack into columns with short interplanar spacings and hydrogen bonds cross-link the stacks *via* the anions.

Comment

Bifunctional isothiocyanates react with hydrazines to give thiosemicarbazides, which can be cyclized to the corresponding substituted triazolidines (Kutschy, Kristian, Dzurilla & Kováč, 1980; Richter, Klatt, Feuerer & Schulze, 1992). Similar products were also obtained from the reaction of 1-ethoxy-1-isothiocyanatopropane with phenylhydrazines (Bernát, Kristian, Guspanová, Imrich & Bušová, 1997). This reaction has been used to synthesize a triazolidine derivative, (I), with a biologically active acridine skeleton (Abu-Shady, Ragab & Ali, 1990), however, the spectral data of the product were inconsistent with the expected structure. An X-ray structural analysis revealed the product to be the title compound, (II). The synthesis and spectral results have been reported elsewhere (Kristian *et al.*, 1996).

The acridinium ring system of (II) has a similar geometry to most other examples of this moiety. The bond lengths within the outer rings follow the usual pattern of long and short bonds observed in acridines, acridinium cations (Jones & Neidle, 1975) and anthracene (Brock & Dunitz, 1990). This is the pattern expected by merging the four possible Kekulé structures of acridine (Clark, Robinson, Denny & Lee, 1993). The acridinium ring is not completely planar, but forms a shallow and slightly twisted butterfly conformation folded about the C9···N10 axis, with the angle between the planes of the outer rings being 6.20 (14)°. Although acridine (Phillips, 1956; Phillips, Ahmed & Barnes, 1960) and the 9-aminoacridinium cation (Talacki, Carrell & Glusker, 1974) are almost planar, deviations from planarity are often observed and the magnitude of the deviation appears to be related to the degree of substitution (Jones & Neidle, 1975).

The short N1—C9 bond displays considerable double-bond character due to the contribution of the resonance structure (III), consistent with the 9-aminoacridinium cation (Talacki, Carrell & Glusker, 1974), 9-aminoacridine (Chaudhuri, 1983) and most derivatives thereof. An examination of the structures of 17 9-aminoacridine and 11 9-aminoacridinium compounds extracted from the Cambridge Structural Database (October 1996 release; Allen & Kennard, 1993) shows that when the amino N atom of neutral 9-aminoacridine compounds is bonded to another π system, the N1—C9 bond becomes significantly longer [1.40 (1) Å for four compounds *cf.* 1.35 (1) Å for all other neutral 9-aminoacridines]. Similar substituents on 9-aminoacridinium cations, however, have no significant influence on the length of the N1—C9 bond [1.35 (2) Å for four such examples, including the title compound, *cf.* 1.33 (1) Å for all structures with 9-aminoacridinium cations].

The hydrazine side chain is planar from N1 to C13, with a maximum deviation of 0.024 (3) Å. This plane makes an angle of 9.64 (10)° with the mean plane of the acridinium moiety and is tilted towards the convex side of the acridinium ring distortion.