Table 4. *Cytosine ring torsion angles (°) from the X-ray study and the MO calculation, and mean values calculated from entries in the Cambridge Structural Database*[a]

	X-ray study[b]	MO study[b]	Mean[c]
N(1)—C(2)—N(3)—C(4)	6.9 (4)	5.2	0.6 (11)
C(2)—N(3)—C(4)—C(5)	−1.3 (5)	−3.2	0.7 (9)
N(3)—C(4)—C(5)—C(6)	−3.2 (5)	0.4	1.1 (9)
C(4)—C(5)—C(6)—N(1)	1.9 (6)	0.1	0.2 (4)
C(5)—C(6)—N(1)—C(2)	4.0 (5)	2.1	1.1 (8)
C(6)—N(1)—C(2)—N(3)	−8.2 (4)	−4.7	1.4 (13)

References: (*a*) Allen *et al.* (1979); (*b*) this work; (*c*) Taylor & Kennard (1982).

The intensity data were collected at variable scan speeds ranging from 4 to 29° min^{-1} depending on intensity. Stationary backgrounds were counted on both sides of a peak, each for one-half of the scan time. The structure was solved by direct methods and difference Fourier techniques, and refined by blocked-cascade least-squares methods (Sparks, 1961). H atoms were located from a difference Fourier calculation. Non-H atoms were refined with anisotropic and H atoms with isotropic displacement parameters. Calculations were performed on a Data General micro-eclipse desktop model 30 computer. Software used: *SHELXTL* (Sheldrick, 1985) for structure solution, refinement and molecular graphics.

The X-ray data were collected and processed at North Carolina State University, Raleigh, NC. Work at Duke University was supported by the North Carolina Supercomputing Center and by a grant from the American Cancer Society (NP-741) to BRS. We thank Dr Charles Campana of Siemens Industrial Automation for providing Fig. 2.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, torsion angles and charges on —C—C—H and —O—C—H H atoms calculated using Mulliken analysis and *CHELP* have been deposited with the IUCr (Reference: BK1157). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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L-Histidine Methyl Ester Dihydrochloride

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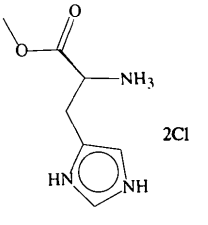
Abstract

The title compound, $C_7H_{13}N_3O_2^{2+}.2Cl^-$, has distances and angles quite similar to those of histidine hydrochloride monohydrate [Donohue & Caron (1964). *Acta Cryst.* **17**, 1178–1180], except for the distances within the ester functionality.

Comment

We have been synthesizing a series of ligands of the form edta(*R*–aa)$_2$, where *R* = CH_3 and CH_2CH_3, in which two amino acid esters (*R*–aa) are amide-linked to an ethylenediaminetetraacetic acid (H_4edta) backbone (Whalen, 1994; Davidson, 1995). During our attempts to make edta(Me–His)$_2$, the solids that were recovered, and recrystallized, after 8 h of reflux proved to be the title compound rather than the desired product.



(I)

Bond lengths and angles are the same within three e.s.d.'s as those of histidine hydrochloride monohydrate (Donohue & Caron, 1964), with the exception of the C—O distances of the ester. In the title compound these distances are pronouncedly different, reflecting the single and double bonds to the O atom, whereas in histidine hydrochloride monohydrate the distances are similar, as is typical of deprotonated carboxylates, CO_2^-.

The crystal is held together, in part, by a network of hydrogen bonds. These distances are typical (Pimentel & McClellan, 1960) and details are included in Table 2.

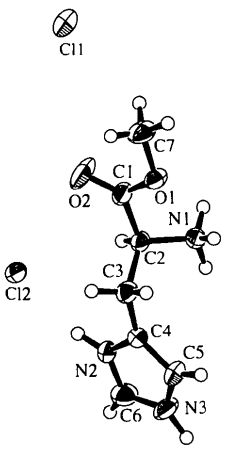


Fig. 1. A perspective drawing of L-histidine methyl ester dihydrochloride with displacement ellipsoids drawn at the 50% probability level.

Experimental

L-Histidine methyl ester dihydrochloride (11.8609 g, 48.99 mmol), ethylenediaminetetraacetic dianhydride (6.3096 g, 24.63 mmol) and triethylamine (12.6594 g, 125.11 mmol) were refluxed for 8 h in 300 ml of tetrahydrofuran. The mixture was allowed to cool. The resulting solids were collected by vacuum filtration and recrystallized from water.

Crystal data

$C_7H_{13}N_3O_2^{2+}.2Cl^-$
$M_r = 242.10$
Monoclinic
$P2_1$
$a = 8.215\ (2)$ Å
$b = 7.105\ (3)$ Å
$c = 9.512\ (2)$ Å
$\beta = 94.54\ (1)°$
$V = 553.4\ (3)$ Å^3
$Z = 2$
$D_x = 1.453$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 19.3–21.3°$
$\mu = 0.566$ mm^{-1}
$T = 294.2$ K
Irregular
0.60 × 0.15 × 0.08 mm
Colorless

Data collection

AFC-7*R* diffractometer
$\omega/2\theta$ scans
$R_{int} = 0.024$
$\theta_{max} = 27.5°$
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.960$, $T_{max} = 0.998$
1473 measured reflections
1380 independent reflections
1090 observed reflections $[I > 3\sigma(I)]$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 9$
$l = -12 \rightarrow 12$
3 standard reflections monitored every 150 reflections
intensity decay: 1.25% (correction applied)

Refinement

Refinement on F
$R = 0.0327$
$wR = 0.0344$
$S = 1.872$
1090 reflections
127 parameters
H-atom parameters not refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max} = 0.014$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	U_{eq}
Cl1	0.21602 (9)	0.067 (2)	−0.58895 (8)	0.0451 (2)
Cl2	0.81079 (8)	0.152 (2)	0.07582 (7)	0.0366 (2)
O1	0.7951 (2)	0.056 (2)	−0.4878 (2)	0.0366 (5)
O2	0.6591 (2)	0.073 (2)	−0.2945 (2)	0.0714 (9)
N1	1.0433 (3)	−0.126 (2)	−0.3414 (2)	0.0328 (6)
N2	1.1807 (2)	0.138 (2)	0.0026 (2)	0.0343 (6)
N3	1.4346 (2)	0.130 (2)	−0.0344 (3)	0.0461 (7)
C1	0.7814 (3)	0.050 (2)	−0.3498 (3)	0.0378 (8)
C2	0.9456 (3)	0.016 (2)	−0.2675 (3)	0.0314 (7)
C3	1.0414 (3)	0.196 (2)	−0.2381 (3)	0.0349 (8)
C4	1.1885 (3)	0.165 (2)	−0.1407 (3)	0.0307 (6)
C5	1.3493 (3)	0.158 (2)	−0.1630 (3)	0.0405 (7)
C6	1.3297 (3)	0.119 (2)	0.0639 (3)	0.0455 (10)
C7	0.6414 (3)	0.084 (2)	−0.5729 (3)	0.053 (1)

Table 2. *Selected geometric parameters (Å, °)*

O1—C1	1.327 (4)	N3—C5	1.375 (5)
O1—C7	1.458 (4)	N3—C6	1.323 (5)
O2—C1	1.182 (4)	C1—C2	1.524 (5)
N1—C2	1.496 (5)	C2—C3	1.518 (5)
N2—C4	1.384 (4)	C3—C4	1.479 (5)
N2—C6	1.320 (4)	C4—C5	1.356 (4)
N2···Cl2	3.172 (2)	N1···Cl1^{i}	3.157 (9)
N3···Cl2^{i}	3.188 (2)	N1···Cl1^{ii}	3.084 (14)
C1—O1—C7	114.6 (3)	C1—C2—C3	112.6 (4)
C4—N2—C6	109.6 (3)	C2—C3—C4	112.2 (4)
C5—N3—C6	108.8 (3)	N2—C4—C3	122.6 (3)
O1—C1—O2	125.3 (4)	N2—C4—C5	105.7 (3)
O1—C1—C2	111.9 (3)	C3—C4—C5	131.8 (3)
O2—C1—C2	122.8 (3)	N3—C5—C4	107.5 (3)
N1—C2—C1	110.6 (3)	N2—C6—N3	108.4 (3)
N1—C2—C3	111.3 (3)		

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

The absolute configuration was fixed by the use of L-histidine in the 'synthesis'. Inversion of the structure and refinement of the D configuration gave a slightly poorer agreement ($R = 0.0329$, $wR = 0.0346$ and $S = 1.88$).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction:

TEXSAN (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

We are grateful to the Kresge Foundation for providing the funds for the purchase of the diffractometer used in this work.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1149). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Diacetylmorphine Polymorph

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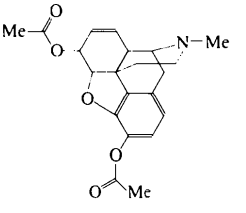
Abstract

The title compound, 7,8-didehydro-4,5-epoxy-17-methylmorphinan-3,6-diyl diacetate, $C_{21}H_{23}NO_5$, was crystallized from a solution of its hydrochloride and sodium acetate. Unlike prior reports in which crystals were hexagonal shaped (orthorhombic) and in space group $P2_12_12_1$, the crystals in the present determination grew as large prisms (monoclinic) and were in space group $P2_1$.

Comment

The addition of sodium acetate to a solution of the hydrochloride of diacetylmorphine induces crystallization of the free base which, along with the morphology of the resulting crystals, has been used as a test to identify diacetylmorphine (Clarke, 1969). This method of crystallization was used by Canfield, Barrick & Giessen (1979) for the first reported crystal structure (orthorhombic, $P2_12_12_1$) of heroin. In this report, we describe a new polymorph of heroin, (I).



(I)

The new heroin polymorph formed as a monoclinic $P2_1$ crystal with two molecules in the asymmetric unit (Fig. 1). These two molecules differ mainly with respect to the conformations of the two acetoxy side chains on atoms C3 and C6, with the largest differences occurring for the C3 side chain. The torsion angle for this functional group (C18—O1—C3—C4) is 86.0 (7)° and the equivalent angle in the second molecule is −94.2 (8)°. The torsion angles of the other acetoxy group (C20—O4—C6—C5) in each of the two molecules agree better, with values of −83.5 (6) and −83.1 (7)°; however, as shown by the superposition of the two molecules in Fig. 2, these acetoxy groups are displaced with respect to each other due to the displacement of atom C6*A* with respect to C6. As expected, the polycyclic ring systems of the two molecules are nearly identical. A comparison of the two ring systems showed a maximum deviation of 0.323 Å at atom C6 and an average r.m.s. deviation of 0.119 Å.

A comparision of the diacetylmorphine structure found in this study with the previously published structure resulted in a 0.114 or 0.054 Å r.m.s. deviation for the polycyclic ring systems (for the two molecules in Fig. 1). The only significant deviation from the previously published structure is in the conformations of the acetoxy side chains at atoms C3 and C6. The conformations are nearly identical to those shown in Fig. 1(*a*), and therefore the differences noted between the two molecules in the new polymorph accurately describe the differences between the molecule shown in Fig. 1(*b*) and the structure reported by Canfield *et al.* (1979).

The unit-cell packing shows similarities to that of the orthorhombic structure (see the supplementary material for a packing diagram), for which interactions between the carbonyl O atoms and the methyl groups of neighboring acetoxy groups were reported, with interatomic