DL-Histidine DL-tartrate

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Key indicators

Single-crystal X-ray study

T = 295 K

Mean σ(C–C) = 0.002 Å

R factor = 0.043

wR factor = 0.118

Data-to-parameter ratio = 15.3

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

The crystal structure of DL-histidine DL-tartrate, $C_6H_{10}N_3O_2^+ \cdot C_4H_5O_6^-$, has been determined as part of an ongoing study of the fundamental effects of chirality on salt formation and hydrates. Discrete single-enantiomer chains of histidine are linked in two dimensions by hydrogen bonds to a racemic pair of tartrate molecules.
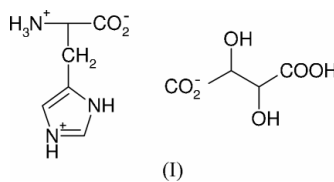
Comment

This study was undertaken to identify the effects of chirality on the formation of salts, specifically the way chirality may affect hydration, as a result of interactions between a chiral drug and a chiral counter-ion. DL-Histidine and DL-tartrate samples were purchased from Fluka and used in the crystallization. The asymmetric unit of the title compound, (I), contains one molecule of histidine as a monocation (protonated at the amine and imidazole N atoms and deprotonated at the carboxylic acid) and the tartrate as a monoanion (Fig. 1).

(I)

The histidines form chains of single enantiomers (Fig. 2) linked along the *b* axis by hydrogen bonds from the NH group of the imidazole ring to a carboxyl O atom of the next histidine, similar to those described by Suresh & Vijayan (1987). The tartrate anions form dimers containing one D- and one L-tartrate ion in each pair (Fig. 2). The dimers are formed by means of a carboxylic acid O atom bonding to a neighbouring tartrate utilizing a side OH group [2.817 (2) Å]. Each histidine molecule in a chain is linked to the next chain below (viewed down the *a* axis in Fig. 2) by a single hydrogen bond from a carboxyl O atom to an NH group of the ammonium group [2.749 (2) Å]. The tartrates link the chains of histidine in two dimensions to create a three-dimensional hydrogen-bond network.

Experimental

A 5 ml saturated aqueous solution of DL-histidine was mixed with a 5 ml saturated aqueous solution of DL-tartaric acid and the vial was covered with a pierced film. This was placed in a larger glass vial containing 25 ml of methanol, sealed, and allowed to stand for three weeks at room temperature.

organic papers

Crystal data

$C_6H_{10}N_3O_2^+ \cdot C_4H_5O_6^-$
$M_r = 305.25$
Monoclinic, $P2_1/c$
$a = 4.9695 (5)$ Å
$b = 13.4392 (12)$ Å
$c = 19.2749 (18)$ Å
$\beta = 90.253 (2)°$
$V = 1287.3 (2)$ Å^3
$Z = 4$

$D_x = 1.575$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2967
  reflections
$\theta = 1.9–28.0°$
$\mu = 0.14$ mm^{-1}
$T = 295 (2)$ K
Needle, colourless
$0.50 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD
  diffractometer
Thin-slice ω scans
Absorption correction: multi-scan
  (SADABS; Sheldrick, 1997;
  Blessing, 1995)
  $T_{min} = 0.843$, $T_{max} = 0.990$
7512 measured reflections

2967 independent reflections
2207 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 28.0°$
$h = -6 \rightarrow 6$
$k = -17 \rightarrow 17$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.118$
$S = 1.02$
2967 reflections
194 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$A\cdots$O8	0.86	1.93	2.7689 (19)	166
N1—H1$\cdots$O2^i	0.86	1.84	2.6871 (19)	169
N3—H3$A\cdots$O2^{ii}	0.89	1.87	2.7532 (18)	173
N3—H3$B\cdots$O7^{iii}	0.89	2.09	2.7937 (18)	135
N3—H3$B\cdots$O6^{iii}	0.89	2.35	3.1374 (18)	147
N3—H3$C\cdots$O7^{ii}	0.89	1.85	2.7178 (18)	164
O3—H3$D\cdots$O1^{iv}	0.82	1.77	2.5856 (17)	173
O5—H5$A\cdots$O4^v	0.82	2.11	2.8174 (19)	145
O5—H5$A\cdots$O4	0.82	2.30	2.7015 (19)	111
O6—H6$\cdots$O8^{vi}	0.82	1.92	2.7152 (18)	162

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

The unit-cell dimensions and angles were compared to those reported for the parent histidine enantiomers by Edington & Harding (1974) and Madden *et al.* (1972). All H atoms were placed geometrically [C—H = 0.93–0.98, N—H = 0.86–0.89 and O—H = 0.82 Å; U_{iso}(H) = 1.2 or 1.5 times U_{eq}(parent atom)] and refined using a riding model.

Data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics:
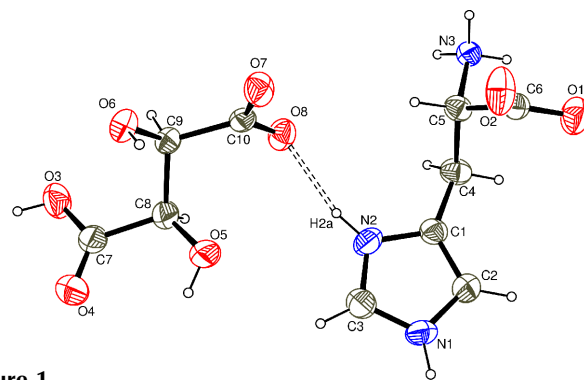

Figure 1
ORTEP-3 (Farrugia, 1997) plot of the asymmetric unit of (I) ($Z = 4$), with displacement ellipsoids drawn at the 50% probability level.
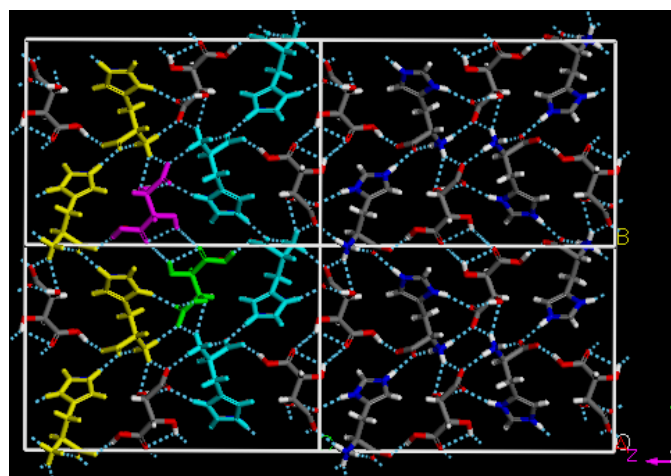

Figure 2
Hydrogen-bonding motifs for D-tartrate (green), L-histidine (yellow), D-histidine (blue) and L-tartrate (pink).

ORTEP-3 (Farrugia, 1997) and *Materials Studio* (Accelrys, 2001); software used to prepare material for publication: *SHELXL*97.

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supporting information

DL-**Histidine** DL-**tartrate**

M. N. Johnson and N. Feeder

(I)

Crystal data

$C_6H_{10}N_3O_2{}^+ \cdot C_4H_5O_6{}^-$	$F(000) = 640$
$M_r = 305.25$	$D_x = 1.575$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P2ybc	Cell parameters from 2967 reflections
$a = 4.9695$ (5) Å	$\theta = 1.9–28.0°$
$b = 13.4392$ (12) Å	$\mu = 0.14$ mm^{-1}
$c = 19.2749$ (18) Å	$T = 295$ K
$\beta = 90.253$ (2)°	Needle, colourless
$V = 1287.3$ (2) Å^3	$0.50 \times 0.10 \times 0.10$ mm
$Z = 4$	

Data collection

Bruker SMART APEX CCD diffractometer	7512 measured reflections
Radiation source: fine-focus sealed tube	2967 independent reflections
Graphite monochromator	2207 reflections with $I > 2\sigma(I)$
Detector resolution: 67 pixels mm^{-1}	$R_{int} = 0.023$
Thin–slice ω scans	$\theta_{max} = 28.0°$, $\theta_{min} = 1.9°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1997; Blessing, 1995)	$h = -6 \rightarrow 6$
	$k = -17 \rightarrow 17$
$T_{min} = 0.843$, $T_{max} = 0.990$	$l = -25 \rightarrow 25$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.044$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.118$	
$S = 1.02$	H-atom parameters constrained
2967 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2]$
194 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.44$ e Å^{-3}
	$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
C1	0.1685 (3)	0.73187 (12)	0.66501 (9)	0.0318 (4)
C2	0.2198 (4)	0.77519 (13)	0.72645 (10)	0.0386 (4)
H2	0.1342	0.7610	0.7681	0.046*
C3	0.4909 (4)	0.84349 (13)	0.65168 (10)	0.0372 (4)
H3	0.6224	0.8836	0.6319	0.045*
C4	−0.0369 (4)	0.65675 (12)	0.64434 (10)	0.0358 (4)
H4A	−0.1390	0.6824	0.6052	0.043*
H4B	−0.1609	0.6473	0.6825	0.043*
C5	0.0819 (3)	0.55634 (11)	0.62459 (9)	0.0298 (4)
H5	0.2238	0.5664	0.5901	0.036*
C6	0.1981 (3)	0.49876 (11)	0.68674 (8)	0.0286 (4)
C7	0.8407 (4)	0.92923 (12)	0.38923 (9)	0.0392 (4)
C8	0.6893 (4)	0.85823 (12)	0.43616 (9)	0.0376 (4)
H8	0.4990	0.8773	0.4372	0.045*
C9	0.7135 (3)	0.75243 (11)	0.40876 (8)	0.0281 (4)
H9	0.6004	0.7473	0.3671	0.034*
C10	0.6010 (3)	0.67992 (12)	0.46299 (8)	0.0273 (3)
N1	0.4190 (3)	0.84348 (11)	0.71715 (8)	0.0377 (4)
H1	0.4868	0.8807	0.7491	0.045*
N2	0.3426 (3)	0.77602 (10)	0.61863 (8)	0.0364 (4)
H2A	0.3533	0.7621	0.5752	0.044*
N3	−0.1363 (3)	0.49502 (9)	0.59342 (7)	0.0282 (3)
H3A	−0.2652	0.4854	0.6246	0.042*
H3B	−0.0698	0.4365	0.5803	0.042*
H3C	−0.2046	0.5264	0.5567	0.042*
O1	0.0532 (3)	0.48152 (10)	0.73684 (7)	0.0461 (4)
O2	0.4328 (3)	0.46847 (11)	0.68080 (7)	0.0495 (4)
O3	0.7603 (3)	0.92187 (10)	0.32456 (7)	0.0481 (4)
H3D	0.8607	0.9543	0.2996	0.072*
O4	1.0095 (3)	0.98561 (11)	0.41035 (7)	0.0591 (4)
O5	0.7946 (4)	0.85996 (10)	0.50444 (7)	0.0601 (5)
H5A	0.8650	0.9141	0.5119	0.090*
O6	0.9796 (2)	0.72979 (9)	0.38935 (6)	0.0358 (3)
H6	1.0753	0.7274	0.4241	0.054*
O7	0.7460 (3)	0.60922 (9)	0.48094 (6)	0.0404 (3)
O8	0.3696 (2)	0.69787 (9)	0.48593 (6)	0.0373 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0383 (9)	0.0256 (8)	0.0315 (9)	0.0024 (7)	−0.0027 (7)	0.0006 (7)
C2	0.0436 (10)	0.0401 (10)	0.0320 (9)	−0.0066 (8)	0.0008 (8)	−0.0019 (7)
C3	0.0361 (9)	0.0333 (9)	0.0423 (11)	−0.0002 (7)	0.0060 (8)	−0.0009 (8)
C4	0.0367 (10)	0.0292 (8)	0.0412 (10)	0.0039 (7)	−0.0063 (8)	−0.0017 (7)
C5	0.0297 (8)	0.0269 (8)	0.0327 (9)	−0.0001 (6)	−0.0035 (7)	0.0009 (7)
C6	0.0304 (9)	0.0273 (8)	0.0279 (8)	0.0006 (7)	−0.0017 (7)	−0.0003 (6)
C7	0.0551 (11)	0.0276 (9)	0.0348 (10)	0.0012 (8)	0.0075 (9)	0.0001 (7)
C8	0.0510 (11)	0.0294 (9)	0.0326 (9)	0.0001 (8)	0.0089 (8)	0.0012 (7)
C9	0.0297 (8)	0.0304 (8)	0.0241 (8)	0.0012 (6)	0.0000 (6)	−0.0001 (6)
C10	0.0312 (9)	0.0283 (8)	0.0224 (8)	−0.0025 (7)	−0.0038 (6)	−0.0038 (6)
N1	0.0421 (9)	0.0369 (8)	0.0343 (8)	−0.0071 (6)	−0.0015 (7)	−0.0104 (6)
N2	0.0470 (9)	0.0360 (8)	0.0263 (7)	0.0054 (6)	0.0017 (6)	−0.0049 (6)
N3	0.0316 (7)	0.0257 (7)	0.0272 (7)	0.0007 (5)	−0.0008 (6)	0.0008 (5)
O1	0.0492 (8)	0.0501 (8)	0.0392 (8)	0.0112 (6)	0.0127 (6)	0.0072 (6)
O2	0.0344 (7)	0.0703 (9)	0.0438 (8)	0.0153 (6)	0.0063 (6)	0.0235 (7)
O3	0.0602 (9)	0.0482 (8)	0.0358 (8)	−0.0120 (7)	0.0006 (6)	0.0124 (6)
O4	0.0872 (12)	0.0490 (8)	0.0411 (8)	−0.0283 (8)	0.0049 (8)	−0.0044 (7)
O5	0.1103 (13)	0.0425 (8)	0.0275 (7)	−0.0259 (8)	0.0044 (8)	−0.0045 (6)
O6	0.0343 (7)	0.0434 (7)	0.0297 (6)	0.0033 (5)	0.0052 (5)	0.0001 (5)
O7	0.0489 (7)	0.0368 (7)	0.0354 (7)	0.0086 (6)	0.0026 (6)	0.0093 (5)
O8	0.0314 (7)	0.0471 (7)	0.0335 (7)	−0.0024 (5)	0.0036 (5)	−0.0007 (5)

Geometric parameters (Å, º)

C1—C2	1.343 (3)	C7—C8	1.517 (2)
C1—N2	1.381 (2)	C8—O5	1.414 (2)
C1—C4	1.489 (2)	C8—C9	1.522 (2)
C2—N1	1.362 (2)	C8—H8	0.9800
C2—H2	0.9300	C9—O6	1.4092 (19)
C3—N1	1.313 (2)	C9—C10	1.536 (2)
C3—N2	1.329 (2)	C9—H9	0.9800
C3—H3	0.9300	C10—O7	1.2407 (19)
C4—C5	1.522 (2)	C10—O8	1.2574 (19)
C4—H4A	0.9700	N1—H1	0.8600
C4—H4B	0.9700	N2—H2A	0.8600
C5—N3	1.487 (2)	N3—H3A	0.8900
C5—C6	1.537 (2)	N3—H3B	0.8900
C5—H5	0.9800	N3—H3C	0.8900
C6—O1	1.229 (2)	O3—H3D	0.8200
C6—O2	1.241 (2)	O5—H5A	0.8200
C7—O4	1.200 (2)	O6—H6	0.8200
C7—O3	1.311 (2)		
C2—C1—N2	105.53 (15)	C7—C8—C9	109.92 (14)
C2—C1—C4	131.08 (17)	O5—C8—H8	109.2

N2—C1—C4	123.29 (15)	C7—C8—H8	109.2
C1—C2—N1	108.13 (16)	C9—C8—H8	109.2
C1—C2—H2	125.9	O6—C9—C8	111.69 (14)
N1—C2—H2	125.9	O6—C9—C10	112.87 (13)
N1—C3—N2	107.93 (15)	C8—C9—C10	109.09 (13)
N1—C3—H3	126.0	O6—C9—H9	107.7
N2—C3—H3	126.0	C8—C9—H9	107.7
C1—C4—C5	113.69 (14)	C10—C9—H9	107.7
C1—C4—H4A	108.8	O7—C10—O8	125.43 (15)
C5—C4—H4A	108.8	O7—C10—C9	117.58 (14)
C1—C4—H4B	108.8	O8—C10—C9	116.99 (14)
C5—C4—H4B	108.8	C3—N1—C2	109.12 (15)
H4A—C4—H4B	107.7	C3—N1—H1	125.4
N3—C5—C4	108.02 (13)	C2—N1—H1	125.4
N3—C5—C6	107.87 (12)	C3—N2—C1	109.29 (14)
C4—C5—C6	113.34 (14)	C3—N2—H2A	125.4
N3—C5—H5	109.2	C1—N2—H2A	125.4
C4—C5—H5	109.2	C5—N3—H3A	109.5
C6—C5—H5	109.2	C5—N3—H3B	109.5
O1—C6—O2	124.38 (16)	H3A—N3—H3B	109.5
O1—C6—C5	119.22 (15)	C5—N3—H3C	109.5
O2—C6—C5	116.30 (14)	H3A—N3—H3C	109.5
O4—C7—O3	125.44 (16)	H3B—N3—H3C	109.5
O4—C7—C8	122.86 (17)	C7—O3—H3D	109.5
O3—C7—C8	111.69 (16)	C8—O5—H5A	109.5
O5—C8—C7	111.23 (15)	C9—O6—H6	109.5
O5—C8—C9	107.99 (14)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O8	0.86	1.93	2.7689 (19)	166
N1—H1···O2[i]	0.86	1.84	2.6871 (19)	169
N3—H3A···O2[ii]	0.89	1.87	2.7532 (18)	173
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Symmetry codes: (i) −x+1, y+1/2, −z+3/2; (ii) x−1, y, z; (iii) −x+1, −y+1, −z+1; (iv) x+1, −y+3/2, z−1/2; (v) −x+2, −y+2, −z+1; (vi) x+1, y, z.