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(*R*,*S*)-3-Carboxy-2-(isoquinolinium-2-yl)-propanoate monohydrate

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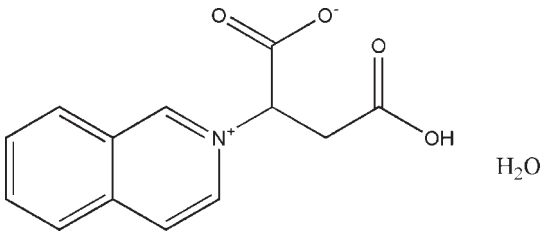
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.011 Å; R factor = 0.076; wR factor = 0.222; data-to-parameter ratio = 9.3.

The title compound, $C_{13}H_{11}NO_4\cdot H_2O$, is a monohydrate of a betaine exhibiting a positively charged *N*-substituted isoquinoline group and a deprotonated carboxyl group. In the crystal, molecules are connected *via* short O—H···O hydrogen bonds between protonated and deprotonated carboxyl groups into chains of either *R* or *S* enantiomers along [001]. These chains are additionally connected by hydrogen bonding between water molecules and the deprotonated carboxy groups of neighbouring molecules.

Related literature

For the structure of a co-crystal of a quinoline derivative betaine, see: Szafran *et al.* (2002) and for the structure of a 4-dithiocarboxylisoquinoline betaine, see: Matthews *et al.* (1973). For possible applications of isoquinoline derivatives, see: Katritsky & Pozharskii (2000). For the preparation of the title compound, see: Flett & Gardner (1952).



Experimental

Crystal data

$C_{13}H_{11}NO_4\cdot H_2O$
M_r = 263.24
Monoclinic, *Pc*
a = 10.1030 (15) Å
b = 8.0706 (8) Å
c = 7.8911 (10) Å
β = 104.282 (14)°
V = 623.53 (14) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 295 K
0.43 × 0.19 × 0.17 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
7142 measured reflections
1659 independent reflections
994 reflections with $I > 2\sigma(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.076
$wR(F^2)$ = 0.222
S = 1.02
1659 reflections
178 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H1···O2	0.86 (6)	2.05 (6)	2.851 (7)	156 (6)
O5—H2···O2^{i}	0.86 (6)	2.08 (7)	2.874 (7)	153 (6)
O4—H4···O1^{ii}	0.82	1.70	2.518 (7)	172

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PLATON* (Spek, 2009) and *PARST* (Nardelli, 1995).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2195).

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(*R*,*S*)-3-Carboxy-2-(isoquinolinium-2-yl)propanoate monohydrate

Vladimir Stilinović, Leo Frkanec and Branko Kaitner

S1. Comment

Isoquinoline derivatives are of interest in synthesizing new fungicides, insecticides, textile assistants, corrosion inhibitors, dye stabilizers, and pharmaceuticals (Katritsky & Pozharskii, 2000) The molecular structure of I is given in Figure 1. The molecule of 3-carboxy-2-isoquinolinium-2-ylpropanoate is a betaine, i.e. a zwitterion containing a quaternary nitrogen atom and a deprotonated carboxyl group. It is the first betaine derived from isoquinoline to be structurally characterised, the only two similar compounds being a quinoline derivative (Szafran *et al.*, 2002) and a 4-dithiocarboxylisoquinoline derivative (Matthews *et al.*, 1973)

The compound crystallises in the space group P*c* with two formula units per unit cell. Molecules of 3-carboxy-2-isoquinolinium-2-ylpropanoate are connected *via* strong hydrogen bonds between protonated and deprotonated carboxyl groups (O4—H4···O1 2.518 (7) Å, (*x*, *y*, -1+*z*)) along the *c* axis. Water molecules bridge two deprotonated carboxyl groups of neighbouring molecules along chains (O5—H2···O2 2.874 (7) Å, (*x*, 2- *y*, 1/2 + *z*) and O5—H1···O2 2.851 (7) Å). Chains consist of either *R* or *S* enantiomers and each chain is interconnected by water molecules to a neighbouring chain in which the molecules are of opposite chirality, thus forming double chains about the glide plane.

S2. Experimental

The title compound (I) was prepared according to a method described earlier (Flett & Gardner, 1952). Separate solutions are prepared of isoquinoline (1.17 ml; 10 mmol) and maleic acid (1.16 g; 10 mmol) in anhydrous ether. Upon mixing, isoquinolinium maleate precipitates. This precipitate is separated by filtration, washed, and dried. It is then rapidly heated to its melting point at 103 °C and held at this temperature for a few minutes. Rapid conversion to the betaine takes place. The betaine is then purified by dissolving it in hot water and treatment with animal charcoal. The solution was set aside for the formation of crystals, yield is 79 %. Crystals suitable for crystallographic study were grown from a solution of (I) in water by slow evaporation at room temperature.

S3. Refinement

The hydrogen atoms of the water molecule were located in the difference Fourier map and refined isotropically with the O–H distance restrained to 0.857 (2) Å. All other H atoms were placed geometrically and included in the refinement in the riding-model approximation with U_{iso} = 1.2 U_{eq} for hydrogen atoms bonded to carbon and U_{iso} = 1.5 U_{eq} for the hydroxyl hydrogen. To the quinolinium subunit rigid bond restraints were applied. Since there are no heavy atoms in the structure the Flack parameter was meaningless due to a large s.u., and the Friedel pairs were merged for the final refinement.

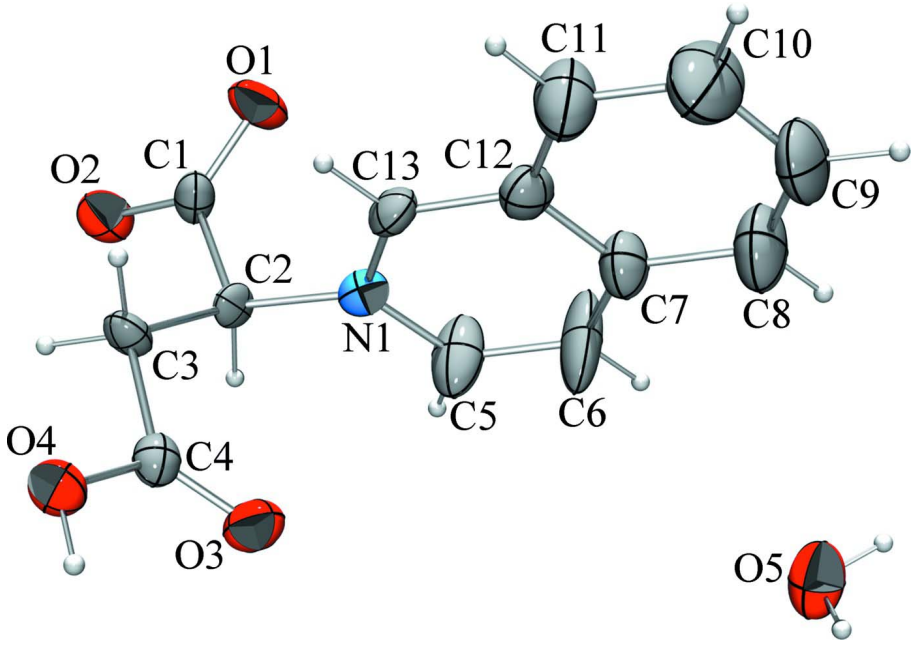

Figure 1

View of (I) with the atom labeling scheme. Displacement ellipsoids of are shown at 30% probability. Hydrogen atoms are shown as spheres of arbitrary radii.

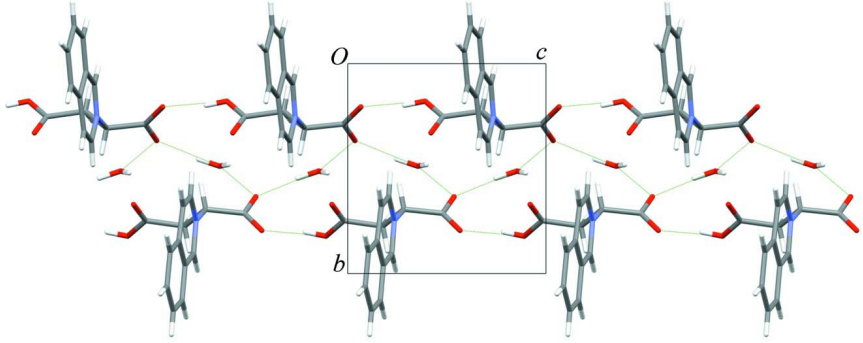

Figure 2

Crystal packing of (I) viewed along the *x* axis.

(*R*,*S*)-3-Carboxy-2-(isoquinolin-2-ium-2-yl)propanoate monohydrate

Crystal data

$C_{13}H_{11}NO_4·H_2O$
$M_r = 263.24$
Monoclinic, *Pc*
Hall symbol: P -2yc
$a = 10.1030\ (15)$ Å
$b = 8.0706\ (8)$ Å
$c = 7.8911\ (10)$ Å
$\beta = 104.282\ (14)°$
$V = 623.53\ (14)$ Å^3
$Z = 2$
$F(000) = 276$
$D_x = 1.402$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 275 reflections
$\theta = 4.6–52.0°$
$\mu = 0.11$ mm^{-1}
$T = 295$ K
Prism, colourless
0.43 × 0.19 × 0.17 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scan
7142 measured reflections
1659 independent reflections
994 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 29°$, $\theta_{min} = 3.9°$
$h = -13 \rightarrow 13$
$k = -11 \rightarrow 11$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.076$
$wR(F^2) = 0.222$
$S = 1.02$
1659 reflections
178 parameters
6 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1361P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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}
O5	0.9214 (4)	0.9884 (8)	0.9683 (6)	0.0817 (17)
H1	0.865 (6)	0.928 (9)	0.895 (8)	0.085*
H2	0.885 (7)	1.014 (11)	1.052 (7)	0.086*
O3	0.5000 (5)	0.8301 (5)	0.0404 (6)	0.0581 (12)
O1	0.5719 (5)	0.7025 (7)	0.6870 (6)	0.0664 (14)
O4	0.6768 (5)	0.6788 (6)	0.0104 (6)	0.0576 (12)
H4	0.6439	0.6955	−0.094	0.086*
C2	0.5675 (6)	0.8088 (7)	0.4031 (6)	0.0340 (11)
H2A	0.5661	0.9273	0.3756	0.041*
N1	0.4242 (5)	0.7538 (5)	0.3583 (6)	0.0375 (10)
C4	0.6005 (6)	0.7514 (6)	0.1025 (7)	0.0372 (12)
C1	0.6317 (6)	0.7933 (7)	0.6011 (7)	0.0384 (12)
O2	0.7403 (5)	0.8672 (6)	0.6568 (6)	0.0584 (12)
C12	0.2584 (7)	0.5400 (7)	0.3023 (7)	0.0448 (13)
C3	0.6546 (6)	0.7251 (7)	0.2928 (7)	0.0415 (13)
H3A	0.7469	0.7684	0.3277	0.05*

H3B	0.6589	0.6071	0.3167	0.05*
C13	0.3918 (7)	0.5934 (7)	0.3442 (8)	0.0446 (13)
H13	0.4616	0.5153	0.3632	0.054*
C7	0.1528 (8)	0.6561 (9)	0.2716 (11)	0.0632 (18)
C6	0.1918 (8)	0.8250 (10)	0.287 (2)	0.115 (5)
H6	0.1246	0.9064	0.2687	0.137*
C10	0.0902 (11)	0.3265 (12)	0.251 (2)	0.121 (5)
H10	0.0679	0.2145	0.2447	0.146*
C8	0.0157 (8)	0.6063 (11)	0.2240 (15)	0.088 (3)
H8	−0.0545	0.6839	0.1992	0.105*
C11	0.2251 (9)	0.3727 (10)	0.2954 (16)	0.093 (3)
H11	0.2935	0.2928	0.3209	0.112*
C9	−0.0115 (9)	0.4417 (12)	0.2152 (14)	0.089 (3)
H9	−0.102	0.4065	0.184	0.107*
C5	0.3220 (8)	0.8692 (9)	0.3285 (14)	0.083 (3)
H5	0.3444	0.9812	0.3373	0.099*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O5	0.058 (3)	0.088 (4)	0.093 (4)	0.004 (3)	0.009 (3)	−0.029 (3)
O3	0.070 (3)	0.058 (3)	0.044 (2)	0.011 (3)	0.010 (2)	0.012 (2)
O1	0.087 (4)	0.088 (3)	0.0270 (19)	−0.019 (3)	0.020 (2)	0.006 (2)
O4	0.074 (3)	0.068 (3)	0.032 (2)	0.004 (2)	0.0153 (19)	−0.004 (2)
C2	0.050 (3)	0.035 (3)	0.0162 (18)	−0.003 (2)	0.0079 (19)	0.0013 (18)
N1	0.049 (3)	0.030 (2)	0.031 (2)	0.0015 (19)	0.0078 (18)	−0.0013 (17)
C4	0.045 (3)	0.036 (3)	0.030 (3)	−0.011 (2)	0.008 (2)	−0.013 (2)
C1	0.040 (3)	0.042 (3)	0.034 (3)	0.000 (2)	0.009 (2)	0.002 (2)
O2	0.056 (3)	0.077 (3)	0.037 (2)	−0.020 (2)	0.0025 (18)	0.002 (2)
C12	0.045 (3)	0.047 (3)	0.039 (3)	−0.004 (3)	0.003 (2)	0.004 (2)
C3	0.048 (3)	0.043 (3)	0.029 (3)	0.000 (3)	0.002 (2)	0.007 (2)
C13	0.049 (4)	0.035 (3)	0.048 (3)	0.002 (3)	0.007 (3)	0.003 (2)
C7	0.043 (4)	0.054 (4)	0.090 (5)	0.003 (3)	0.013 (3)	−0.012 (3)
C6	0.037 (5)	0.043 (4)	0.244 (15)	0.004 (3)	−0.002 (6)	−0.030 (6)
C10	0.066 (6)	0.059 (5)	0.215 (15)	−0.022 (4)	−0.010 (7)	0.032 (7)
C8	0.039 (4)	0.073 (5)	0.142 (8)	−0.008 (4)	0.006 (4)	−0.010 (6)
C11	0.067 (6)	0.042 (4)	0.152 (9)	−0.010 (4)	−0.008 (6)	−0.001 (5)
C9	0.047 (5)	0.085 (6)	0.126 (8)	−0.029 (4)	0.003 (4)	−0.006 (5)
C5	0.045 (4)	0.034 (3)	0.157 (8)	0.008 (3)	0.004 (4)	−0.024 (4)

Geometric parameters (Å, º)

O5—H1	0.86 (6)	C12—C7	1.396 (9)
O5—H2	0.86 (6)	C3—H3A	0.97
O3—C4	1.195 (7)	C3—H3B	0.97
O1—C1	1.250 (7)	C13—H13	0.93
O4—C4	1.320 (7)	C7—C8	1.402 (11)
O4—H4	0.82	C7—C6	1.416 (11)

C2—N1	1.471 (7)	C6—C5	1.324 (11)
C2—C3	1.538 (7)	C6—H6	0.93
C2—C1	1.543 (6)	C10—C9	1.364 (13)
C2—H2A	0.98	C10—C11	1.372 (12)
N1—C13	1.333 (7)	C10—H10	0.93
N1—C5	1.368 (8)	C8—C9	1.354 (12)
C4—C3	1.481 (7)	C8—H8	0.93
C1—O2	1.231 (7)	C11—H11	0.93
C12—C13	1.375 (8)	C9—H9	0.93
C12—C11	1.389 (10)	C5—H5	0.93

H1—O5—H2	109 (7)	H3A—C3—H3B	107.8
C4—O4—H4	109.5	N1—C13—C12	122.0 (5)
N1—C2—C3	113.5 (4)	N1—C13—H13	119
N1—C2—C1	111.2 (4)	C12—C13—H13	119
C3—C2—C1	112.4 (4)	C12—C7—C8	121.1 (7)
N1—C2—H2A	106.4	C12—C7—C6	116.5 (7)
C3—C2—H2A	106.4	C8—C7—C6	122.3 (7)
C1—C2—H2A	106.4	C5—C6—C7	121.3 (7)
C13—N1—C5	119.2 (6)	C5—C6—H6	119.3
C13—N1—C2	121.3 (5)	C7—C6—H6	119.3
C5—N1—C2	119.5 (5)	C9—C10—C11	121.2 (8)
O3—C4—O4	124.2 (5)	C9—C10—H10	119.4
O3—C4—C3	123.8 (5)	C11—C10—H10	119.4
O4—C4—C3	112.0 (5)	C9—C8—C7	118.0 (8)
O2—C1—O1	126.7 (5)	C9—C8—H8	121
O2—C1—C2	116.0 (5)	C7—C8—H8	121
O1—C1—C2	117.2 (5)	C10—C11—C12	119.3 (8)
C13—C12—C11	121.9 (6)	C10—C11—H11	120.3
C13—C12—C7	119.5 (6)	C12—C11—H11	120.3
C11—C12—C7	118.6 (7)	C8—C9—C10	121.7 (8)
C4—C3—C2	113.0 (4)	C8—C9—H9	119.2
C4—C3—H3A	109	C10—C9—H9	119.2
C2—C3—H3A	109	C6—C5—N1	121.4 (7)
C4—C3—H3B	109	C6—C5—H5	119.3
C2—C3—H3B	109	N1—C5—H5	119.3

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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