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1-Carboxymethyl-3-iodo-1-pyridinium–iodide–(3-iodo-1-pyridinio)acetate (1/1/1)

Peter G. Jones,* Berta Cots Carrasquer and Eva-Maria Zerbe

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

Correspondence e-mail: p.jones@tu-bs.de

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The title compound, $C_7H_7I_2NO_2^+ \cdot I^- \cdot C_7H_6I_2NO_2$, crystallizes with $Z' = \frac{1}{2}$; the iodide anion lies on a twofold axis, and in the cation/zwitterion adduct the acidic H atom is disordered over an inversion centre. The residues are linked to form zigzag chains in the overall direction [103] by I···I interactions between anion and cation, and by classical O—H···O hydrogen bonds. Weak hydrogen bonds C—H···O link the chains to form layers parallel to $(30\overline{1})$.

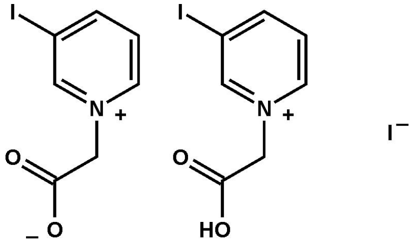
Key indicators

Single-crystal X-ray study
T = 133 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.029
wR factor = 0.052
Data-to-parameter ratio = 24.3

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

Comment

We are interested in secondary bonding contacts (classical and 'weak' hydrogen bonds, and halogen–halogen contacts) in structures of pyridine derivatives. A brief summary of our relevant publications is given in Jones & Lozano (2004).



(I)

The title compound, (I), arose as an unexpected product from the reaction between 3-iodopyridine and iodoacetic acid; a simple adduct had been expected, but clearly the pyridine N atom, acting as a nucleophile, had displaced the iodide from iodoacetic acid. The compound is formally an adduct of the

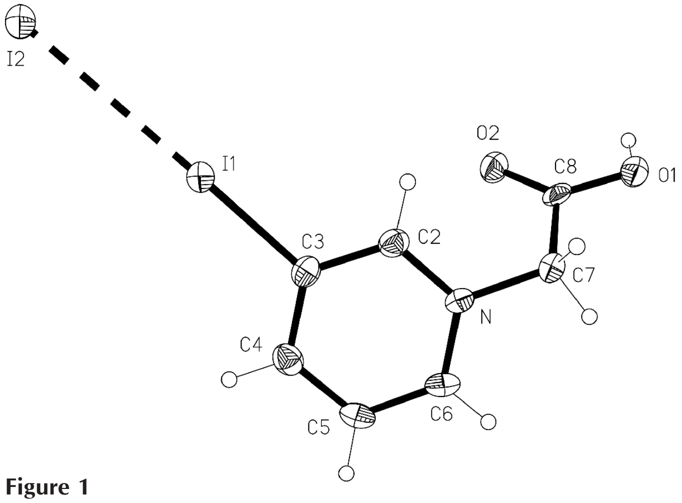


Figure 1
The asymmetric unit of the title compound in the crystal structure. Displacement ellipsoids are drawn at the 50% probability level. The H-atom radii are arbitrary.

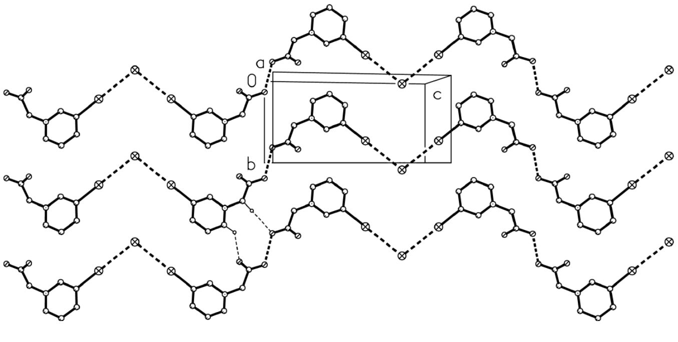


Figure 2
Packing diagram of the title compound with a view direction perpendicular to (30$\overline{1}$). H atoms have been omitted. Thick dashed lines indicate O—H···O hydrogen bonds and iodine–iodine interactions. Thin dashed lines indicate one of each type of 'weak' hydrogen bond (H6···O2 and H7*A*···O2).

neutral zwitterion (3-iodo-1-pyridinio)acetate, the cation 1-carboxymethyl-3-iodo-1-pyridinium, and iodide anion in a 1:1:1 ratio. The asymmetric unit is shown in Fig. 1. The iodide ion lies on a twofold axis ($\frac{1}{4}$, y, $\frac{1}{4}$), but there is only one independent 1-carboxymethyl-3-iodo-1-pyridinium moiety, linked to another *via* the inversion centre ($\frac{1}{2}$, 0, 1); the acidic H atom is accordingly disordered over this centre. Dimensions of the 'carboxylic acid' group C8/O1/O2 should therefore be interpreted with caution, because they in fact represent a superposition of a carboxylate and a carboxylic acid group.

Within the asymmetric unit, the iodo substituent I1 of the pyridine ring and iodide anion I2 are linked by a short contact of 3.4443 (4) Å, with a C—I1···I2 angle of 175.99 (8)°. The carboxylate group is rotated with respect to the ring plane by an interplanar angle of 56.4 (1)°. Dimensions of the pyridine system may be regarded as normal; a search of the Cambridge Structural Database (Version 5.26; Allen, 2002) revealed 97 hits for the pyridinioacetate system (including any ring substituents and all varieties of the carboxylate group), with 183 individual values and derived mean values of 1.470 (13) Å for the N—CH_2 bond length and 120.5 (1)° for the ring C—N—C bond angle.

The crystal packing (Fig. 2) involves two main types of contact. First, the iodide ion bridges two pyridine ring systems *via* an I1···I2···I1^{i} grouping with an angle at I2 of 103.066 (13)°. Secondly, the carboxylate/carboxylic acid groups are linked by a classical hydrogen bond, with O···O = 2.474 (5) Å. The net effect is to form zigzag chains of residues in the overall direction [103] *via* the twofold axes ($\frac{1}{2} - x$, y, $\frac{1}{2} - z$) and the inversion centres ($\frac{1}{2}$, 0, 0) and (0, 0, $\frac{1}{2}$). Neighbouring chains are related by the b translation and linked by the 'weak' hydrogen bonds H6···O2 and H7*A*···O1 (Table 2), and thus form layers parallel to (30$\overline{1}$). Layers are linked in the third dimension by the weak hydrogen bonds H5···O2, H2···I2 and H7*B*···I2.

Experimental

3–Iodopyridine (55.1 mg) and iodoacetic acid (50 mg, molar ratio 1:1) were dissolved in ethanol (5 ml). The combined solution was allowed to stand for several weeks. Small crystals of the title compound formed in poor yield.

Crystal data

$C_7H_7INO_2^+\cdot I^-\cdot C_7H_6INO_2$
$M_r = 653.96$
Monoclinic, $P2/n$
$a = 10.9984$ (8) Å
$b = 6.3486$ (4) Å
$c = 13.2439$ (12) Å
$\beta = 99.768$ (4)°
$V = 911.34$ (12) Å^3
$Z = 2$
$D_x = 2.383$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 4228 reflections
$\theta = 2$–30.5°
$\mu = 5.16$ mm^{-1}
$T = 133$ (2) K
Prism, colourless
0.11 × 0.05 × 0.05 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\min} = 0.622$, $T_{\max} = 0.772$
11241 measured reflections
2648 independent reflections
2049 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 30.0°$
$h = -15 \rightarrow 15$
$k = -8 \rightarrow 8$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.052$
$S = 0.95$
2648 reflections
109 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0229P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.92$ e Å^{-3}
$\Delta\rho_{\min} = -1.03$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

I2—I1^{i}	3.4443 (4)	C6—N	1.349 (4)
C2—N	1.356 (4)	N—C7	1.481 (4)
C3—I1	2.112 (3)		
I1—I2—I1^{i}	103.066 (13)	C6—N—C7	119.5 (3)
C6—N—C2	121.5 (3)	C2—N—C7	119.0 (3)
C2—N—C7—C8	−57.8 (4)	N—C7—C8—O2	4.4 (4)

Symmetry code: (i) $\frac{1}{2} - x, y, \frac{1}{2} - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H01···O1^{ii}	0.83 (2)	1.73 (4)	2.474 (5)	150 (8)
C7—H7*A*···O1^{iii}	0.99	2.50	3.451 (4)	162
C5—H5···O2^{iv}	0.95	2.54	3.349 (4)	143
C6—H6···O2^{v}	0.95	2.34	3.062 (4)	132
C2—H2···I2^{vi}	0.95	3.26	3.960 (3)	132
C7—H7*B*···I2^{vi}	0.99	2.94	3.758 (3)	140

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

The half-occupied H-atom site bonded to nitrogen was identified in a difference synthesis and refined with a distance restraint of 0.84 (2) Å. Other H atoms were included using a riding model with fixed C—H bond lengths of 0.95 (pyridine) or 0.99 Å (methylene); $U_{\rm iso}$(H) values were fixed at 1.2 times the $U_{\rm eq}$ value of the parent C atom. Major features of residual electron density lie near the I atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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