

$\beta$ -Pyridinium dichloroiodide

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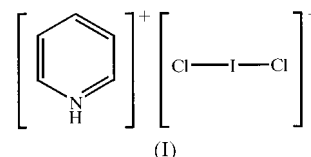
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The  $\beta$  modification of pyridinium dichloroiodide,  $C_5H_6N^+ \cdot Cl_2I^-$ , was obtained as yellow crystals by the reaction of  $(C_5NH_5)AuCl_3$ ,  $C_5H_6N^+ \cdot Cl^-$  and  $I_2$  in a vacuum-sealed ampoule. The dichloroiodide ion is nearly symmetric and linear with I—Cl bond lengths of 2.544 (3) and 2.550 (3) Å and a Cl—I—Cl angle of 179.68 (12)°.

## Comment

The dichloroiodide ion has been characterized in many compounds showing different forms (Bandoli *et al.*, 1978; Grebe *et al.*, 1995). Tucker reported the  $\alpha$  modification of pyridinium dichloroiodide as trigonal, space group  $R\bar{3}m$ , with  $a = 6.165$  (4) Å,  $\alpha = 82.45$  (6)° and  $Z = 1$  (Tucker & Kroon, 1973). We present (I), the  $\beta$  modification of this compound, which crystallizes in the orthorhombic space group  $Pnma$  with  $a = 8.0390$  (5),  $b = 7.694$  (16),  $c = 14.130$  (2) Å and  $Z = 4$ .

The title compound is formed during the reaction of  $(C_5NH_5)AuCl_3$ ,  $C_5H_6N^+ \cdot Cl^-$  and  $I_2$  in a sealed glass ampoule. We also observed the formation of elemental gold. Crystals of good quality were obtained by subsequent sublimation. The asymmetric unit contains a half dichloroiodide anion located on a mirror plane and a half pyridinium cation off a mirror plane.



The packing diagram (Fig. 1) shows the pyridinium cation packed in stacks along the  $a$  axis. The dichloroiodide anion packs with the Cl—I—Cl units parallel in a zigzag pattern along the  $b$  axis between the pyridinium stacks with a spacing of 4.3931 (10) Å between the anions. The cation–anion (H—Cl) distance of 2.86–2.94 Å (Table 2) is rather shorter than the sum of the van der Waals radii (Pauling, 1960), suggesting that the cation–anion interactions control the packing.

In the  $\beta$ -modification, the deviation of the Cl—I—Cl bond angle [179.68 (12)°] from linearity is not significant. The bond lengths of I—Cl1 = 2.544 (3) and I—Cl2 = 2.550 (3) Å can be considered symmetric and have values similar to that already found in similar anions (2.54–2.69 Å) (Bandoli *et al.*, 1978; Grebe *et al.*, 1995). In agreement with another similar structure we are assuming that the cation is sixfold disordered; we have been unable to distinguish an ordered  $C_5H_6N^+$  ion (Tucker & Kroon, 1973). The pyridinium ion is treated as six symmetry-related CH groups (occupancy = 5/6) and six related NH groups (occupancy = 1/6). Selected bond distances and angles are given in Table 1.

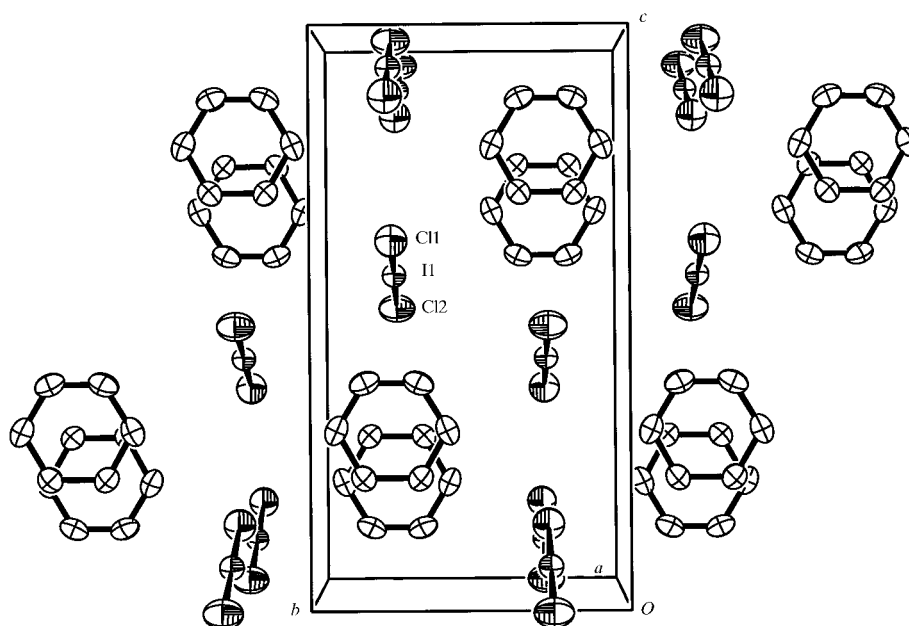


Figure 1

View of the title structure with the Cl and I atoms labelled. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

$\beta$ -Pyridinium dichloriodide was formed when  $(C_5NH_5)AuCl_3$ ,  $C_5H_6N^+ \cdot Cl^-$  and  $I_2$  in the molar ratio 1:1:4 were heated in a sealed glass ampoule (diameter = 1.2 cm, length = 20 cm). To obtain high quality crystals, it is essential that the temperature is increased slowly between 373 and 523 K. After cooling,  $\beta$ -pyridinium dichloriodide deposits as yellow single crystals. Elemental analysis (calculated/found): C 21.60/23.07, H 2.16/2.34, N 5.03/5.07%.

Crystal data

$C_5H_6N^+ \cdot Cl_2I^-$  Mo  $K\alpha$  radiation  
 $M_r = 277.91$  Cell parameters from 25 reflections  
 Orthorhombic,  $Pnma$   $\theta = 5.3\text{--}16.3^\circ$   
 $a = 8.0390(5) \text{ \AA}$   $\mu = 4.195 \text{ mm}^{-1}$   
 $b = 7.6940(16) \text{ \AA}$   $T = 208(2) \text{ K}$   
 $c = 14.130(2) \text{ \AA}$  Needle, yellow  
 $V = 874.0(2) \text{ \AA}^3$   $0.20 \times 0.10 \times 0.05 \text{ mm}$   
 $Z = 4$   
 $D_x = 2.112 \text{ Mg m}^{-3}$

Data collection

CAD-4 diffractometer  $\theta_{\max} = 27.96^\circ$   
 $\omega/2\theta$  scans  $h = -1 \rightarrow 10$   
 Absorption correction:  $\psi$  scan  $k = 0 \rightarrow 10$   
 (North *et al.*, 1968)  $l = -18 \rightarrow 1$   
 $T_{\min} = 0.660$ ,  $T_{\max} = 0.811$  3 standard reflections  
 1378 measured reflections every 200 reflections  
 1129 independent reflections intensity decay: 5.3%  
 $R_{\text{int}} = 0.075$

Refinement

Refinement on  $F^2$  H atoms constrained  
 $R[F^2 > 2\sigma(F^2)] = 0.057$   $w = 1/[\sigma^2(F_o^2) + (0.0715P)^2]$   
 $wR(F^2) = 0.141$  where  $P = (F_o^2 + 2F_c^2)/3$   
 $S = 1.046$   $(\Delta/\sigma)_{\max} < 0.001$   
 1129 reflections  $\Delta\rho_{\max} = 1.92 \text{ e \AA}^{-3}$   
 46 parameters  $\Delta\rho_{\min} = -1.11 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

I1—C1	2.544 (3)	C1—C1 <sup>i</sup>	1.384 (17)
I1—C2	2.550 (3)	C2—C3	1.363 (11)
C1—C2	1.361 (11)	C3—C3 <sup>i</sup>	1.312 (18)
C11—I1—C12	179.68 (12)	C1—C2—C3	120.0 (8)
C2—C1—C1 <sup>i</sup>	119.2 (5)	C3 <sup>i</sup> —C3—C2	120.9 (5)

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

Table 2

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C1—H1 <sup>i</sup> $\cdots$ Cl1 <sup>i</sup>	0.93	2.91	3.566 (9)	129
C1—H1 <sup>i</sup> $\cdots$ Cl2	0.93	2.90	3.512 (8)	125
C3—H3 <sup>i</sup> $\cdots$ Cl1 <sup>ii</sup>	0.93	2.94	3.570 (9)	127
C3—H3 <sup>i</sup> $\cdots$ Cl2 <sup>iii</sup>	0.93	2.86	3.527 (9)	130

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1994); cell refinement: *CAD-4 Software*; data reduction: *HELENA* (Spek, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1276). Services for accessing these data are described at the back of the journal.

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