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## Key indicators

Single-crystal X-ray study  
 $T = 300\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$   
 $R$  factor = 0.043  
 $wR$  factor = 0.159  
Data-to-parameter ratio = 18.1For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

## Pyrrolidinium chloranilate

In the title compound,  $2\text{C}_4\text{H}_{10}\text{N}^+\cdot\text{C}_6\text{Cl}_2\text{O}_4^{2-}$ , the pyrrolidinium and chloranilate ions are connected by  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds and arranged in an alternating manner to give an infinite molecular tape.

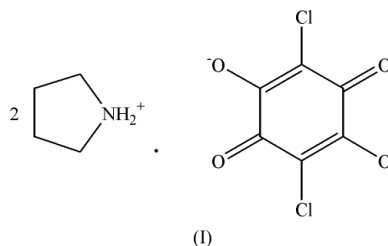
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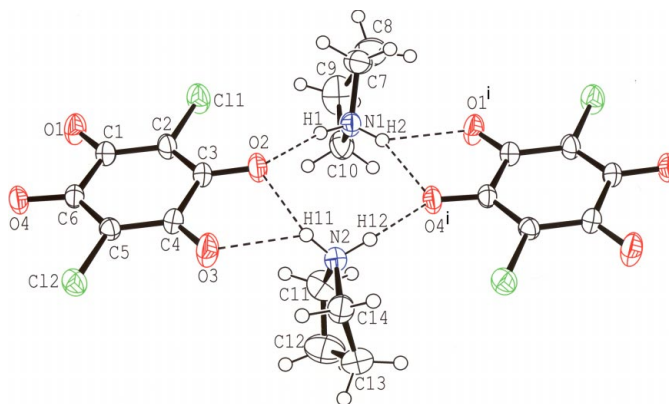
Online 15 May 2004

## Comment

The title compound, (I), was investigated as part of a study on  $D-\text{H}\cdots A$  hydrogen bonding ( $D = \text{N}, \text{O}$ , or  $\text{C}$ ;  $A = \text{N}, \text{O}, \text{Cl}$ ) in chloranilic acid–amine 1:1 and 1:2 systems (Ishida & Kashino, 1999*a,b,c*, 2000, 2001, 2002; Ishida *et al.*, 2001; Fukunaga & Ishida, 2003; Fukunaga *et al.*, 2003). Crystal structures of the chloranilic acid–secondary amine 1:1 system have been analyzed for the morpholinium, diethylammonium and piperidinium salts (Ishida & Kashino, 1999*c*, 2000; Fukunaga & Ishida, 2003), but the structure of the chloranilic acid–secondary amine 1:2 system has not yet been reported. In the present study, we prepared the 1:2 salt, (I), using pyrrolidine as a counter-base and determined its crystal structure.



In (I), the asymmetric unit is composed of  $2\text{C}_4\text{H}_8\text{NH}_2^+\cdot\text{C}_6\text{O}_4\text{Cl}_2^{2-}$ ; an acid–base interaction involving a proton transfer is observed between the chloranilic acid and



**Figure 1**  
ORTEP-3 (Farrugia, 1997) drawing of (I), with the atom-labeling scheme. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level.  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds are indicated by dashed lines [symmetry code: (i)  $x - 1, y, z$ ].

pyrrolidine (Fig. 1). The chloranilate ion shows a characteristic structure having four short C—C bonds [1.382 (3)–1.416 (3) Å] and two extremely long C—C bonds [1.540 (3) and 1.544 (3) Å], which is explainable in terms of the double  $\pi$  system of the anion (Andersen, 1967; Benckekroun & Savariault, 1995). The chloranilate and pyrrolidinium ions are connected by N—H $\cdots$ O hydrogen bonds (Table 2) and arranged in an alternating manner to give a molecular tape running along the *a* axis (Fig. 2). The tapes are stacked along the *b* axis, such that the chloranilate ions related by an inversion center are stacked through  $\pi$ – $\pi$  interactions, with an interplanar spacing of 3.346 Å and a centroid offset of 3.209 Å ( $Cg\cdots Cg = 4.636$  Å; *Cg* is the centroid of each anion).

The pyrrolidinium cation, which is isoelectronic with cyclopentane, is expected to have ring flexibility as high as cyclopentane. Molecular-orbital calculations for the isolated cation in the gas phase showed that the twist form ( $C_2$  form) is the stable conformation and that the envelope on N atom form ( $C_s$  form) is a saddle point of the first order (Ishida, 2000). Other twist conformations and envelope on C-atom conformations have not been optimized as stationary points. The difference in the electronic energy between the  $C_2$  and  $C_s$  forms calculated at the HF/6–31G(*d,p*) level is 2.0 kJ mol $^{-1}$ , which is small compared to the energies of intermolecular interactions in the solid. In the present salt, the N1–C7–C8–C9–C10 cation ring is close to the  $C_2$  form, while the N2–C11–C12–C13–C14 ring is close to the envelope on C13 form.

## Experimental

Crystals were obtained by slow evaporation of an acetonitrile solution of pyrrolidine and chloranilic acid in a 2:1 molar ratio.

### Crystal data

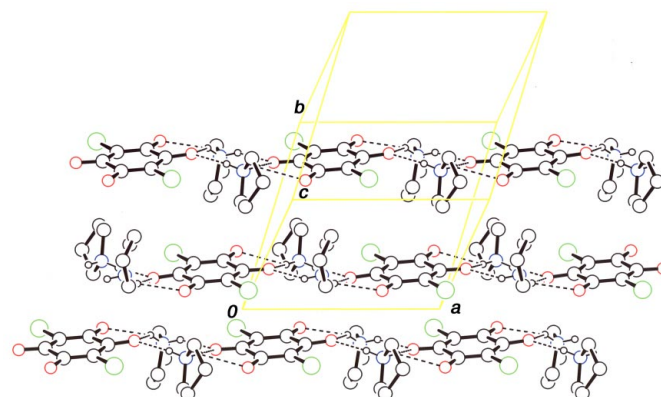
$2C_4H_{10}N^+ \cdot C_6Cl_2O_4^{2-}$	$Z = 2$
$M_r = 351.23$	$D_x = 1.486$ Mg m $^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.337$ (3) Å	Cell parameters from 25 reflections
$b = 9.601$ (4) Å	$\theta = 11.2$ – $11.8^\circ$
$c = 9.947$ (5) Å	$\mu = 0.43$ mm $^{-1}$
$\alpha = 68.18$ (3) $^\circ$	$T = 300$ K
$\beta = 84.25$ (3) $^\circ$	Prism, dark red
$\gamma = 71.52$ (2) $^\circ$	$0.40 \times 0.20 \times 0.15$ mm
$V = 785.0$ (6) Å $^3$	

### Data collection

Rigaku AFC-5R diffractometer	$R_{int} = 0.014$
$\omega$ – $2\theta$ scans	$\theta_{max} = 27.5^\circ$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$h = -12 \rightarrow 11$
$T_{min} = 0.91$ , $T_{max} = 0.94$	$k = -12 \rightarrow 0$
3821 measured reflections	$l = -12 \rightarrow 11$
3606 independent reflections	3 standard reflections
2522 reflections with $I > 2\sigma(I)$	every 97 reflections
	intensity decay: 1.7%

### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.043$	$w = 1/[\sigma^2(F_o^2) + (0.09P)^2]$
$wR(F^2) = 0.159$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.001$
3606 reflections	$\Delta\rho_{max} = 0.57$ e Å $^{-3}$
199 parameters	$\Delta\rho_{min} = -0.36$ e Å $^{-3}$



**Figure 2**

Packing diagram showing a molecular tape formed via N—H $\cdots$ O hydrogen bonds (shown as dashed lines). H atoms except those attached to N atoms have been omitted for clarity.

**Table 1**

Selected geometric parameters (Å,  $^\circ$ ).

C1—C2	1.746 (3)	C1—C6	1.544 (3)
C2—C5	1.742 (2)	C2—C3	1.382 (3)
O1—C1	1.230 (3)	C3—C4	1.540 (3)
O2—C3	1.256 (3)	C4—C5	1.415 (3)
O3—C4	1.238 (3)	C5—C6	1.384 (3)
O4—C6	1.259 (3)	C7—C8	1.487 (4)
N1—C7	1.495 (3)	C8—C9	1.498 (5)
N1—C10	1.495 (3)	C9—C10	1.502 (5)
N2—C11	1.497 (3)	C11—C12	1.482 (4)
N2—C14	1.499 (3)	C12—C13	1.510 (5)
C1—C2	1.416 (3)	C13—C14	1.516 (4)
C1—C2—C11	117.3 (2)	O2—C3—C4	116.1 (2)
C4—C5—C2	117.4 (2)	O3—C4—C3	116.9 (2)
O1—C1—C6	117.1 (2)	O4—C6—C1	116.1 (2)

**Table 2**

Hydrogen-bonding geometry (Å,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ O2	0.89	1.91	2.791 (3)	169
N1—H2 $\cdots$ O1 $^i$	0.89	2.39	2.962 (3)	122
N1—H2 $\cdots$ O4 $^i$	0.89	1.98	2.824 (3)	158
N2—H11 $\cdots$ O2	0.89	2.12	2.841 (3)	138
N2—H11 $\cdots$ O3	0.89	2.26	2.930 (2)	132
N2—H12 $\cdots$ O4 $^i$	0.89	1.96	2.783 (3)	153

Symmetry code: (i)  $x - 1, y, z$ .

H atoms were treated as riding atoms, with C—H = 0.97 Å and N—H = 0.89 Å.  $U_{iso}(H)$  values were set at  $1.5U_{eq}$  of the parent atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1990); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *TEXSAN for Windows*.

X-ray measurements were made at the X-ray Laboratory of Okayama University.

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