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Key indicators

Single-crystal X-ray study
 $T = 299\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.035
 wR factor = 0.093
Data-to-parameter ratio = 13.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Piperidinium hydrogen chloranilate

In the title compound, $\text{C}_5\text{H}_{10}\text{NH}_2^+\cdot\text{C}_6\text{HO}_4\text{Cl}_2^-$, two chloranilate ions are connected by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds to form a dimeric unit. The piperidinium ions are linked on both sides of the dimer *via* a bifurcated $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond to afford a 2:2 complex of chloranilic acid and piperidine. The 2:2 complexes are linked together to form a hydrogen-bonded molecular tape.

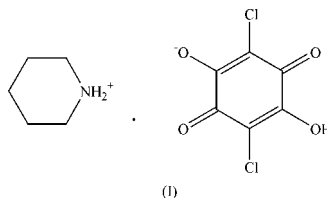
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Comment

The title compound, (I), was investigated as part of a study on $D-\text{H}\cdots A$ hydrogen bonding ($D = \text{N, O, or C}$; $A = \text{N, O, Cl}$) in chloranilic acid–amine 1:1 and 1:2 systems. Chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone), a strong dibasic acid endowed with hydrogen-bond donor as well as acceptor groups, appears particularly attractive as a template for generating tightly bound self-assemblies with polarizable bases (Ishida & Kashino, 1999*a,b,c*, 2000, 2001, 2002; Zaman *et al.*, 1999, 2000). Crystal structures of chloranilic acid–secondary amine 1:1 systems have been analysed for morpholinium and diethylammonium salts (Ishida & Kashino, 1999*c*, 2000). In the morpholinium salt, a chain of chloranilate ions is formed through $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, and morpholinium ions link the two chains through $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds. In the diethylammonium salt, the chloranilic acids form a centrosymmetric dimer through $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, and two diethylammonium ions related by an inversion center link the two dimers by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds to afford an infinite chain.



In (I), the asymmetric unit is composed of $\text{C}_5\text{H}_{10}\text{NH}_2^+\cdot\text{C}_6\text{HO}_4\text{Cl}_2^-$, and an acid–base interaction involving a proton transfer is observed between chloranilic acid and piperidine. Two hydrogen chloranilate ions related by an inversion center are connected by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds and form a dimeric unit as observed in the diethylammonium salt (Fig. 1). Atom H1 is also involved in an intramolecular hydrogen bond with O3. The piperidinium ions are linked on both sides of the dimer *via* bifurcated hydrogen bonds, $\text{N}-\text{H}2\cdots\text{O}1$ and $\text{N}-\text{H}2\cdots\text{O}4$, forming a 2:2 complex of chloranilic acid and piperidine. The 2:2 complexes are linked together by bifurcated hydrogen bonds, $\text{N}-\text{H}3\cdots\text{O}2$ and $\text{N}-\text{H}3\cdots\text{O}3$, to afford a molecular tape running along the [110]

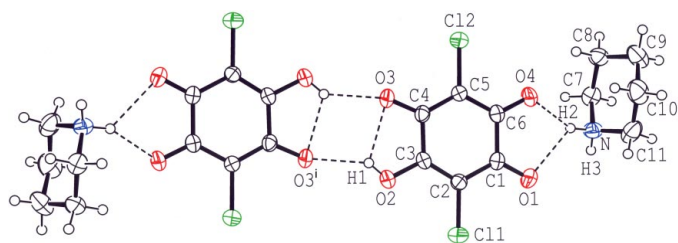


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of (I) with the atom-labeling. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level. O—H...O and N—H...O hydrogen bonds are indicated by dashed lines [symmetry code: (i) $1 - x, -y, -z$].

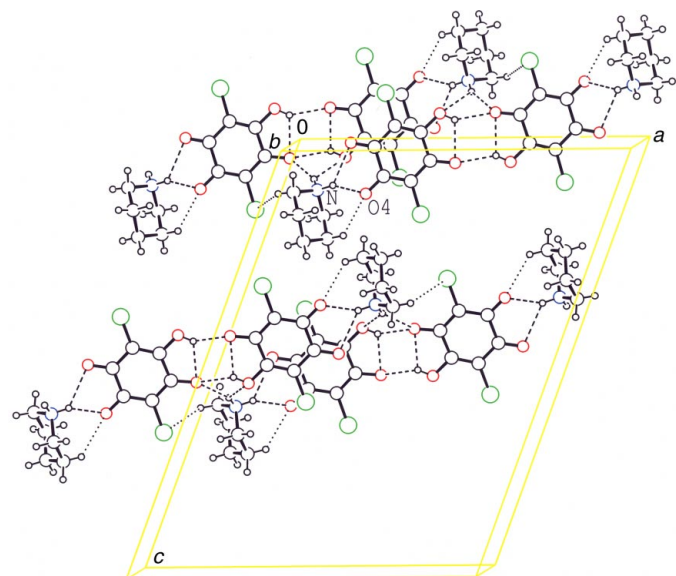


Figure 2
Packing diagram, showing a molecular tape formed via O—H...O and N—H...O hydrogen bonds (shown as dashed lines). C—H...O and C—H...Cl hydrogen bonds are indicated by dotted lines.

direction (Fig. 2). Besides the O—H...O and N—H...O hydrogen bonds, there are C—H...O and C—H...Cl hydrogen bonds within the 2:2 complex and in the tape, respectively (Table 2), but no significant interactions are observed between neighboring tapes.

Experimental

Crystals of (I) were obtained by slow evaporation of an acetonitrile solution of piperidine with chloranilic acid in a 1:1 molar ratio.

Crystal data

$C_5H_{12}N^+ \cdot C_6HCl_2O_4^-$
 $M_r = 294.13$
 Monoclinic, $C2/c$
 $a = 17.263$ (5) Å
 $b = 6.800$ (4) Å
 $c = 22.832$ (8) Å
 $\beta = 110.80$ (2)°
 $V = 2505.5$ (19) Å³
 $Z = 8$

$D_x = 1.559$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 11.7$ – 12.0 °
 $\mu = 0.52$ mm⁻¹
 $T = 299$ K
 Prism, dark purple
 $0.30 \times 0.30 \times 0.25$ mm

Data collection

Rigaku AFC-5R diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{min} = 0.816$, $T_{max} = 0.877$
 3924 measured reflections
 2866 independent reflections
 2029 reflections with $I > 2\sigma(I)$

$R_{int} = 0.028$
 $\theta_{max} = 27.5$ °
 $h = 0 \rightarrow 22$
 $k = -2 \rightarrow 8$
 $l = -29 \rightarrow 27$
 3 standard reflections
 every 97 reflections
 intensity decay: 1.1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.093$
 $S = 1.03$
 2866 reflections
 216 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 2.03P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.01$
 $\Delta\rho_{max} = 0.31$ e Å⁻³
 $\Delta\rho_{min} = -0.27$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient:
 1.4 (3) $\times 10^{-3}$

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-----------|-------------|-----------|-------------|
| C11—C2 | 1.722 (2) | C1—C6 | 1.545 (3) |
| C12—C5 | 1.730 (2) | C2—C3 | 1.347 (3) |
| O1—C1 | 1.216 (2) | C3—C4 | 1.511 (3) |
| O2—C3 | 1.324 (2) | C4—C5 | 1.388 (3) |
| O2—H1 | 0.79 (3) | C5—C6 | 1.410 (3) |
| O3—C4 | 1.259 (2) | C7—C8 | 1.503 (4) |
| O4—C6 | 1.233 (2) | C8—C9 | 1.508 (4) |
| N—C11 | 1.490 (4) | C9—C10 | 1.528 (4) |
| N—C7 | 1.500 (3) | C10—C11 | 1.506 (5) |
| C1—C2 | 1.444 (3) | | |
| O1—C1—C6 | 118.17 (18) | O3—C4—C3 | 115.08 (18) |
| C1—C2—C11 | 118.59 (15) | C4—C5—C12 | 119.71 (15) |
| O2—C3—C4 | 115.44 (17) | O4—C6—C1 | 116.65 (18) |

Table 2

Hydrogen-bonding geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---------------------------|----------|--------------|--------------|----------------|
| O2—H1...O3 | 0.80 (4) | 2.17 (3) | 2.614 (3) | 115 (3) |
| O2—H1...O3 ⁱ | 0.80 (4) | 2.05 (4) | 2.713 (3) | 140 (3) |
| N—H2...O1 | 0.92 (3) | 2.36 (3) | 3.049 (3) | 131 (2) |
| N—H2...O4 | 0.92 (3) | 1.97 (3) | 2.817 (3) | 153 (2) |
| N—H3...O3 ⁱⁱ | 0.84 (3) | 2.21 (3) | 3.000 (3) | 157 (3) |
| N—H3...O2 ⁱⁱⁱ | 0.84 (3) | 2.56 (3) | 3.177 (3) | 131 (3) |
| C7—H5...Cl2 ⁱⁱ | 0.95 (3) | 2.82 (3) | 3.708 (4) | 156 (2) |
| C8—H6...O4 | 0.95 (3) | 2.49 (3) | 3.200 (4) | 132 (2) |

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

H atoms were found in a difference Fourier map and refined isotropically. Refined distances: C—H = 0.86 (3)–1.03 (4), N—H = 0.83 (3) and 0.92 (3), and O—H = 0.79 (3) Å.

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: *ORTEP-3* (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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