$S = 1.075$
1681 reflections
147 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2 + 0.2614P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: *SHELXL*93
Extinction coefficient: 0.040 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters and hydrogen-bonding geometry (Å, °)*

| | | | |
|---|---|---|---|
| S1—O3 | 1.4383 (15) | N1—C1 | 1.333 (2) |
| S1—O1 | 1.4460 (14) | N1—C5 | 1.335 (2) |
| S1—O2 | 1.4564 (14) | N2—C10 | 1.337 (2) |
| S1—C2 | 1.781 (2) | N2—C6 | 1.345 (2) |
| O3—S1—O1 | 115.02 (10) | C1—C2—S1 | 119.58 (13) |
| O3—S1—O2 | 112.42 (9) | C3—C2—S1 | 122.39 (13) |
| O1—S1—O2 | 112.51 (9) | N1—C5—C4 | 122.8 (2) |
| O3—S1—C2 | 105.89 (8) | N1—C5—C6 | 114.87 (15) |
| O1—S1—C2 | 104.44 (8) | N2—C6—C7 | 118.34 (15) |
| O2—S1—C2 | 105.51 (8) | N2—C6—C5 | 116.19 (14) |
| C1—N1—C5 | 116.97 (15) | C10—C9—C8 | 118.8 (2) |
| C10—N2—C6 | 123.35 (15) | N2—C10—C9 | 119.8 (2) |
| N1—C1—C2 | 124.4 (2) | | |

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2···O2$^{i}$ | 0.86 | 2.04 | 2.817 (2) | 149 |

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

All H atoms were located from difference Fourier synthesis and were allowed to refine riding on their parent atoms. It was possible to positionally refine the proton attached to N2, however, as 'free' refinement yielded a position which was close (within experimental error) to that calculated, it was ultimately refined riding on its parent atom.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992). Cell refinement: *CELDIM* in *CAD*-4-*PC Software*. Data reduction: *XCAD* (McArdle & Higgins, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEX* (McArdle, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1080). Services for accessing these data are described at the back of the journal.

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# 1:1 Complexes of chloranilic acid with pyrazine and morpholine: one- and two-dimensional hydrogen-bond networks

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## Abstract

The hydrogen-bonded 1:1 complexes of chloranilic acid (2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone) with pyrazine (1,4-diazine), pyrazine–chloranilic acid (1/1), $C_4H_4N_2 \cdot C_6H_2Cl_2O_4$, (1), and with morpholine, morpholinium chloranilate, $C_4H_{10}NO^+ \cdot C_6HCl_2O_4^-$, (2), were prepared and their crystal structures were determined at room temperature. The two components in (1) are linked by O—H···N hydrogen bonds to form a one-dimensional chain. In (2), molecules of chloranilic acid form an O—H···O hydrogen-bond chain and that of morpholine links the two chains with N—H···O hydrogen bonds, forming the two-dimensional hydrogen-bond network in the crystal.

## Comment

1:1 Complexes of chloranilic acid with pyrazine and morpholine in the solid state were studied using IR data. For both complexes it was reported that a charge transfer accompanied by a proton transfer occurs between the two components, resulting in $C_4H_5N_2^+ \cdot C_6HCl_2O_4^-$ (Issa *et al.*, 1991) and $C_4H_{10}NO^+ \cdot C_6HCl_2O_4^-$ (Habeeb *et al.*, 1995), the anion and the cation of which are held by N—H(N)···O hydrogen bonds. In the present study, we prepared the 1:1 complexes and determined their crystal structures at room temperature to investigate the hydrogen bonds.

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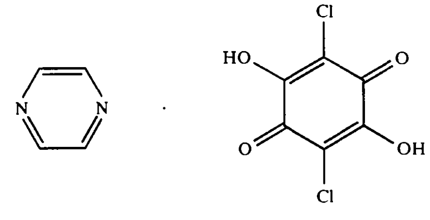
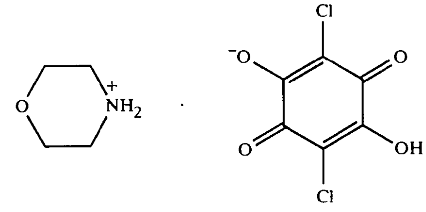


(1)



(2)

In (1), no acid–base interaction involving a proton transfer is observed, which is inconsistent with the result reported by Issa *et al.* (1991). The molecules of chloranilic acid and pyrazine lie around the positions 2*b* and 2*c*, respectively, of the space group $C2/m$ and possess $2/m$ symmetry in the crystal. These molecules are arranged to form an O2—H1···N hydrogen-bond chain along [101] (Fig. 1 and Table 2). The dihedral angle between the planes of chloranilic acid and pyrazine is 90°. The H1 atom is also involved in a weak intermolecular hydrogen bond with O1$^{i}$ [symmetry code: (i) $-x$, $1-y$, $-z$; Table 2]. The C4 atom undergoes strongly anisotropic displacements in the direction perpendicular to the pyrazine ring, suggesting the existence of a large amplitude vibration and/or disordering of the C atoms around a pseudo-$C_2$ axis through the N atoms. However, attempts to resolve the disordered positions were unsuccessful. The shortest contact between the chains is H2···O1$^{ii}$ 2.57 (3) Å [symmetry code: (ii) $\frac{1}{2}-x$, $\frac{3}{2}-y$, $-z$; Table 2], implying that a weak C—H···O interaction exists between the chains.

In (2), two independent chloranilic acid molecules (Fig. 2) having a $\bar{1}$ symmetry are linked by short O—H···O hydrogen bonds [O2···O4 2.512 (2) Å], forming a chain along [221]. The dihedral angle between the planes of the chloranilic acid molecules is 95.6 (1)°. The position of the H atom in the hydrogen bond was found to split into two positions, H1*A* and H1*B*. H1*A* attached to O2 mainly contributes to form the O2—H1*A*···O4 hydrogen bond, while H1*B* attached to O4 participates in the O2···O4 hydrogen bond as well as the intramolecular O4···O3$^{i}$ hydrogen bond [symmetry code: (i) $1-x$, $1-y$, $-z$; Table 4]. Morpholinium ions link the chains of chloranilic acid through N—H2···O4, N—H3···O1$^{ii}$ and N—H3···O2$^{iii}$ hydrogen bonds [symmetry codes: (ii) $x$, $y-1$, $z-1$; (iii) $2-x$, $1-y$, $1-z$; Table 4] (Fig. 3), forming a two-dimensional hydrogen-bond network.

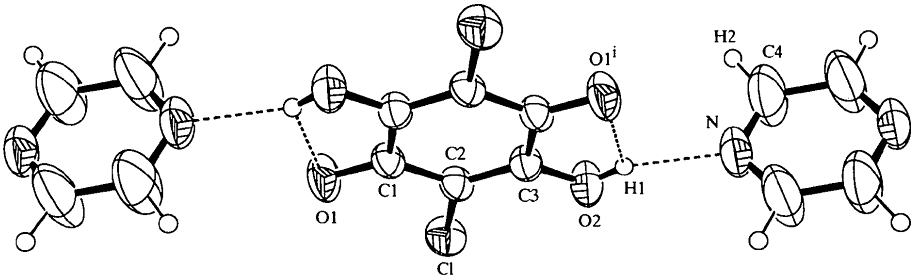


Fig. 1. *ORTEP*-3 (Farrugia, 1997) drawing of (1) forming a one-dimensional hydrogen-bond chain. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are drawn as circles of arbitrary size. Hydrogen bonds are indicated by dashed lines [symmetry code: (i) $-x$, $1-y$, $-z$].

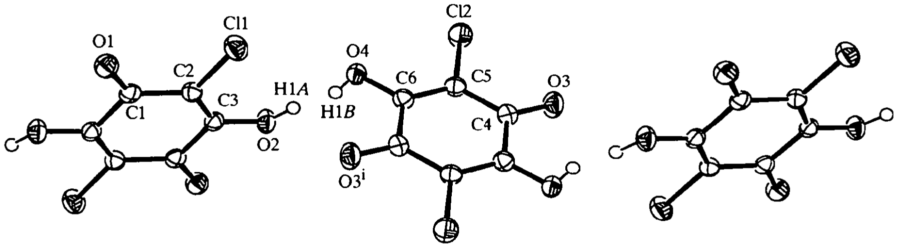


Fig. 2. *ORTEP*-3 (Farrugia, 1997) drawing of the chloranilic acid molecules in (2) forming a one-dimensional hydrogen-bond chain. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are drawn as circles of arbitrary size. Site occupancy factors of H1*A* and H1*B* are 50%. [Symmetry code: (i) $1-x$, $1-y$, $-z$.]

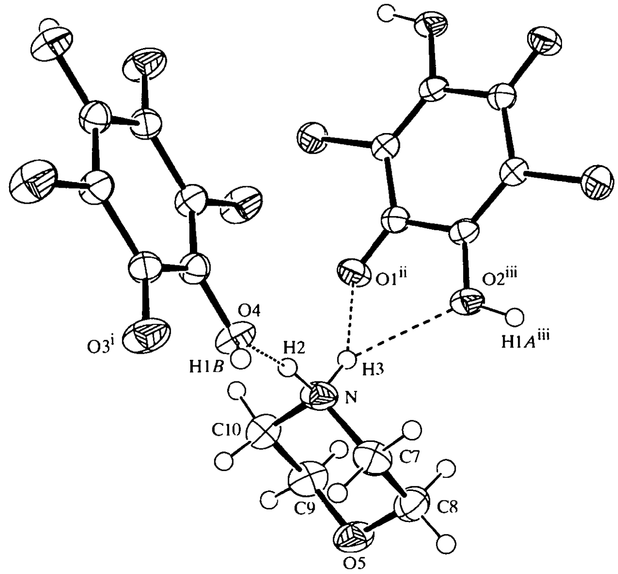


Fig. 3. *ORTEP*-3 (Farrugia, 1997) drawing of the morpholinium ion hydrogen bonded to the chloranilic acid molecules in (2), forming a two-dimensional hydrogen-bond network. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are drawn as circles of arbitrary size. The site-occupancy factors of H1*A* and H1*B* are 50%. N—H···O hydrogen bonds are indicated by dashed lines [symmetry codes: (i) $1 - x$, $1 - y$, $-z$; (ii) $x$, $y - 1$, $z - 1$; (iii) $2 - x$, $1 - y$, $1 - z$].

## Experimental

Crystals of the title complexes were prepared by slow evaporation from acetonitrile solutions of chloranilic acid with pyrazine or morpholine (molar ratio 1:1) at room temperature.

### Compound (1)

*Crystal data*

$C_4H_4N_2{\cdot}C_6H_2Cl_2O_4$
$M_r = 289.07$
Monoclinic
$C2/m$
$a = 8.296\,(5)$ Å
$b = 6.654\,(2)$ Å
$c = 10.993\,(2)$ Å
$\beta = 101.60\,(3)°$
$V = 594.3\,(3)$ Å$^3$
$Z = 2$
$D_x = 1.615$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.0–11.8°$
$\mu = 0.552$ mm$^{-1}$
$T = 297$ K
Prismatic
0.45 × 0.30 × 0.30 mm
Brown

*Data collection*

Rigaku AFC-5*R* diffractometer
$\omega–2\theta$ scans
Absorption correction: $\psi$ scans (North *et al.*, 1968)
$T_{min} = 0.819$, $T_{max} = 0.847$
995 measured reflections
741 independent reflections

625 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 27.48°$
$h = -2 \rightarrow 10$
$k = 0 \rightarrow 8$
$l = -14 \rightarrow 14$
3 standard reflections every 97 reflections intensity decay: 0.27%

*Refinement*

Refinement on $F^2$
$R(F) = 0.037$
$wR(F^2) = 0.084$
$S = 1.76$
739 reflections
60 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + 0.00022|F_o|^2]$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.00$ e Å$^{-3}$
$\Delta\rho_{min} = -0.23$ e Å$^{-3}$
Extinction correction: Zachariasen (1967)
Extinction coefficient: $1.4\,(4) \times 10^{-6}$
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (1)*

| | | | |
|---|---|---|---|
| Cl—C2 | 1.722 (2) | C1—C2 | 1.440 (3) |
| O1—C1 | 1.220 (2) | C1—C3$^{i}$ | 1.508 (3) |
| O2—C3 | 1.312 (3) | C2—C3 | 1.349 (3) |
| N—C4 | 1.282 (3) | C4—C4$^{ii}$ | 1.387 (5) |
| C4—N—C4$^{iii}$ | 114.6 (3) | N—C4—C4$^{ii}$ | 122.7 (1) |

Symmetry codes: (i) $-x$, $1 - y$, $-z$; (ii) $1 - x$, $y$, $1 - z$; (iii) $x$, $1 - y$, $z$.

Table 2. *Hydrogen-bonding and short-contact geometry (Å, °) for (1)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H1···N | 0.81 (3) | 1.98 (3) | 2.719 (3) | 151 (3) |
| O2—H1···O1$^{i}$ | 0.81 (3) | 2.21 (3) | 2.681 (3) | 117 (3) |
| C4—H2···O1$^{ii}$ | 1.03 (4) | 2.57 (3) | 3.320 (4) | 129 (1) |

Symmetry codes: (i) $-x$, $1 - y$, $-z$; (ii) $\frac{1}{2} - x$, $\frac{3}{2} - y$, $-z$.

### Compound (2)

*Crystal data*

$C_4H_{10}NO^+{\cdot}C_6HCl_2O_4^-$
$M_r = 296.11$
Triclinic
$P\bar{1}$
$a = 9.222\,(2)$ Å
$b = 9.241\,(4)$ Å
$c = 8.644\,(4)$ Å
$\alpha = 116.26\,(3)°$
$\beta = 113.55\,(3)°$
$\gamma = 92.65\,(3)°$
$V = 582.9\,(6)$ Å$^3$
$Z = 2$
$D_x = 1.687$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.4–12.0°$
$\mu = 0.569$ mm$^{-1}$
$T = 300$ K
Prismatic
0.30 × 0.30 × 0.20 mm
Brown

*Data collection*

Rigaku AFC-5*R* diffractometer
$\omega–2\theta$ scans
Absorption correction: $\psi$ scans (North *et al.*, 1968)
$T_{min} = 0.833$, $T_{max} = 0.892$
2832 measured reflections
2666 independent reflections

2298 reflections with $I > 2\sigma(I)$
$R_{int} = 0.012$
$\theta_{max} = 27.49°$
$h = 0 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 10$
3 standard reflections every 97 reflections intensity decay: 0.51%

*Refinement*

Refinement on $F^2$
$R(F) = 0.045$
$wR(F^2) = 0.077$
$S = 1.51$
2666 reflections
210 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o) + 0.00027|F_o|^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.33$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.28$ e Å$^{-3}$
Extinction correction: Zachariasen (1967)
Extinction coefficient: 7.3 (5) $\times 10^{-6}$
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (2)*

| | | | |
|---|---|---|---|
| Cl1—C2 | 1.730 (2) | C4—C5 | 1.444 (2) |
| Cl2—C5 | 1.726 (2) | C4—C6$^{ii}$ | 1.522 (2) |
| O1—C1 | 1.222 (2) | C5—C6 | 1.355 (2) |
| O2—C3 | 1.295 (2) | O5—C8 | 1.420 (2) |
| O3—C4 | 1.216 (2) | O5—C9 | 1.424 (2) |
| O4—C6 | 1.299 (2) | N—C7 | 1.489 (2) |
| C1—C2 | 1.439 (2) | N—C10 | 1.492 (2) |
| C1—C3$^{i}$ | 1.527 (2) | C7—C8 | 1.507 (2) |
| C2—C3 | 1.357 (2) | C9—C10 | 1.504 (2) |
| O5—C8—C7 | 110.5 (1) | N—C10—C9 | 109.3 (1) |
| O5—C9—C10 | 111.6 (2) | C7—N—C10 | 111.1 (1) |
| N—C7—C8 | 109.2 (1) | C8—O5—C9 | 110.1 (1) |

Symmetry codes: (i) $2 - x, 2 - y, 2 - z$; (ii) $1 - x, 1 - y, -z$.

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H1*A*···O4 | 0.90 (4) | 1.72 (5) | 2.512 (2) | 145 (4) |
| O2—H1*A*···O3$^{i}$ | 0.90 (4) | 2.45 (5) | 3.067 (2) | 126 (3) |
| O4—H1*B*···O2 | 0.70 (5) | 1.92 (5) | 2.512 (2) | 142 (5) |
| O4—H1*B*···O3$^{i}$ | 0.70 (5) | 2.25 (5) | 2.686 (2) | 122 (4) |
| N—H2···O4 | 0.91 (2) | 1.99 (2) | 2.851 (2) | 157 (2) |
| N—H3···O1$^{ii}$ | 0.93 (2) | 2.07 (2) | 2.928 (2) | 153 (2) |
| N—H3···O2$^{iii}$ | 0.93 (2) | 2.27 (2) | 2.963 (2) | 131 (2) |

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

H atoms were located on difference syntheses and all H atoms except H1*A* and H1*B* in (2) were refined isotropically. The coordinates of H1*A* and H1*B* were refined with an occupancy factor of 0.5; the values of $U_{\rm iso}$ were assumed to be equal to 1.5 times the average value of $U_{\rm eq}$ of O2 and O4 in (2).

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1990); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997). Program(s) used to solve structures: *PATTY* in *DIRDIF*92 (Beurskens *et al.*, 1992) for (1); *SIR*92 (Altomare *et al.*, 1993) for (2). For both compounds, program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1016). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1999). C**55**, 1926–1928

# 1-(2,4-Dinitrophenyl)-3-(2-hydroxyphenyl)-4-methyl-1*H*-pyrazole

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## Abstract

The molecular structure of the title compound, 2-[1-(2,4-dinitrophenyl)-4-methyl-1*H*-pyrazol-3-yl]phenol, $C_{16}H_{12}N_4O_5$, containing a dinitrophenyl and a hydroxyphenyl ring substituted to the pyrazole moiety is one of the products obtained from the reaction of *o*-hydroxy propiophenone 2,4-dinitrophenylhydrazone. The phenyl and pyrazole rings are quite planar. The dihedral angles between the pyrazole and the two phenyl rings are 23.5 (1) and 15.3 (1)°. The interplanar angle between the phenyl ring is 32.6 (1)°. The crystal structure is stabilized by O—H···N-, and O—H···O-type intramolecular hydrogen bonds and the packing of the molecules are stacked by C—H···O-type intermolecular hydrogen bonds.