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Quinoxaline–chloranilic acid (1/1)

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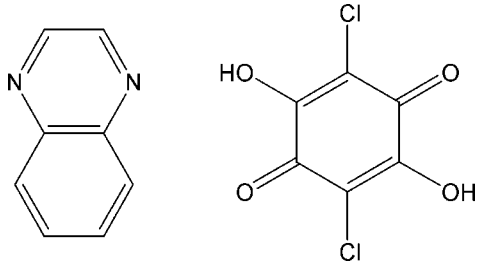
Key indicators: single-crystal X-ray study; T = 95 K; mean σ(C–C) = 0.003 Å; R factor = 0.044; wR factor = 0.102; data-to-parameter ratio = 14.4.

In the crystal structure of the title compound, $C_8H_6N_2\cdot C_6H_2Cl_2O_4$, there are two crystallographically independent chloranilic acid (systematic name: 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) molecules, each of which is located on an inversion center. The quinoxaline ring system makes dihedral angles of 6.09 (9) and 44.50 (9)° with the two chloranilic acid planes. The quinoxaline and the chloranilic acid are connected alternately by O—H···N hydrogen bonds, forming a zigzag chain running along the [20$\bar{1}$] direction. The chains are stacked along the a axis, forming a layer extending parallel to the (010) plane. The layers are further linked by C—H···O hydrogen bonds.

Related literature

For related literature, see: Gotoh *et al.* (2006, 2007); Horiuchi *et al.* (2005); Ishida & Kashino (1999); Prager *et al.* (2005, 2006).



Experimental

Crystal data

$C_8H_6N_2\cdot C_6H_2Cl_2O_4$
M_r = 339.13
Triclinic, $P\bar{1}$
a = 3.7963 (3) Å
b = 7.7760 (7) Å
c = 22.4830 (14) Å
α = 93.444 (3)°
β = 94.338 (3)°
γ = 92.322 (4)°
V = 659.92 (9) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.51 mm^{-1}
T = 95 (1) K
0.48 × 0.43 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.776, T_{max} = 0.950
6457 measured reflections
2974 independent reflections
2314 reflections with $I > 2\sigma(I)$
R_{int} = 0.066

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.102
S = 1.00
2974 reflections
207 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.66 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···N1	0.82 (3)	1.90 (3)	2.683 (2)	159 (3)
O2—H2···O1^{i}	0.82 (3)	2.30 (3)	2.687 (2)	110 (2)
O4—H4···N2	0.84 (5)	1.89 (5)	2.701 (2)	163 (5)
O4—H4···O3^{ii}	0.84 (5)	2.35 (5)	2.691 (2)	105 (4)
C7—H7···O1^{iii}	0.95	2.54	3.191 (3)	126
C8—H8···O3^{ii}	0.95	2.43	3.048 (3)	123
C10—H10···Cl2^{iv}	0.95	2.78	3.560 (2)	140
C11—H11···O3^{iv}	0.95	2.59	3.538 (3)	173

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

Data collection: *PROCESS-AUTO* (Rigaku/MSC, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2054).

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supplementary materials

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Quinoxaline-chloranilic acid (1/1)

K. Gotoh, H. Nagoshi and H. Ishida

Comment

The title compound was prepared in order to extend our study on *D*-H···*A* hydrogen bonding (*D* = N, O, or C; *A* = N, O or Cl) in amine–chloranilic acid 1:1 and 2:1 systems (Gotoh *et al.*, 2006).

The asymmetric unit contains one quinoxaline molecule and two half chloranilic acid molecules. No acid-base interaction involving a proton transfer is observed between the quinoxaline and the chloranilic acid. In the crystal structure, the quinoxaline and the chloranilic acid are linked alternately through two kinds of O—H···N hydrogen bonds to form a zigzag chain running along the [20$\bar{1}$] direction (Fig. 1). Similar chain structures have been observed in the related compounds containing the pyrazine unit, *i.e.*, pyrazine–chloranilic acid (1/1) (Ishida & Kashino, 1999), phenazine–chloranilic acid (1/1) (Horiuchi *et al.*, 2005; Gotoh *et al.*, 2007) and tetramethylpyrazine–chloranilic acid (1/1) (Prager *et al.*, 2005, 2006). The chains are stacked along the *a* axis, forming a layer extending parallel to the (010) plane (Fig. 2). The layers are further linked by C—H···O hydrogen bonds.

Experimental

Single crystals were obtained by slow evaporation from a methanol solution of chloranilic acid (99 mg) and quinoxaline (63 mg).

Refinement

O-bound H atoms were found in a difference Fourier map and refined isotropically (refined distances given in Table 1). C-bound H atoms were positioned geometrically (C—H = 0.95 Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(C).

Figures

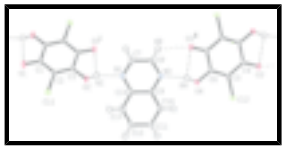

Fig. 1. The molecular structure of the title compound, with 70% probability displacement ellipsoids. The dashed lines indicate hydrogen bonds (symmetry codes as Table 1).

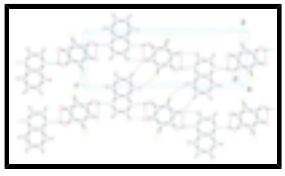

Fig. 2. A partial packing diagram of the title compound, viewed down the *a* axis. The dashed lines indicate hydrogen bonds.

Quinoxaline–chloranilic acid (1/1)

Crystal data

$C_8H_6N_2·C_6H_2Cl_2O_4$	$Z = 2$
$M_r = 339.13$	$F_{000} = 344.00$
Triclinic, $P\overline{1}$	$D_x = 1.707$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71075$ Å
$a = 3.7963$ (3) Å	Cell parameters from 6043 reflections
$b = 7.7760$ (7) Å	$\theta = 3.1$–27.5º
$c = 22.4830$ (14) Å	$\mu = 0.51$ mm^{-1}
$\alpha = 93.444$ (3)º	$T = 95$ (1) K
$\beta = 94.338$ (3)º	Plate, orange
$\gamma = 92.322$ (4)º	0.48 × 0.43 × 0.10 mm
$V = 659.92$ (9) Å^3	

Data collection

Rigaku R-AXIS RAPID diffractometer	2314 reflections with $I > 2\sigma(I)$
Detector resolution: 10.00 pixels mm^{-1}	$R_{int} = 0.066$
ω scans	$\theta_{max} = 27.5$º
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$\theta_{min} = 3.1$º
$T_{min} = 0.776$, $T_{max} = 0.950$	$h = -4 \rightarrow 4$
6457 measured reflections	$k = -10 \rightarrow 10$
2974 independent reflections	$l = -28 \rightarrow 29$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.044$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.102$	$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.001$
2974 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
207 parameters	$\Delta\rho_{min} = -0.66$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.71248 (15)	0.13239 (7)	−0.05495 (2)	0.01197 (14)
Cl2	0.30454 (15)	0.15380 (7)	0.54442 (2)	0.01202 (14)
O1	1.0774 (4)	0.4141 (2)	−0.11448 (6)	0.0123 (3)
O2	0.6729 (4)	0.2726 (2)	0.06970 (6)	0.0123 (4)
O3	−0.0320 (4)	0.4309 (2)	0.61393 (6)	0.0124 (4)
O4	0.3146 (4)	0.2776 (2)	0.42231 (6)	0.0120 (4)
N1	0.6017 (5)	0.3172 (2)	0.18738 (7)	0.0092 (4)
N2	0.4432 (5)	0.3263 (2)	0.30786 (7)	0.0088 (4)
C1	1.0353 (6)	0.4490 (3)	−0.06137 (8)	0.0074 (4)
C2	0.8644 (6)	0.3303 (3)	−0.02377 (8)	0.0077 (4)
C3	0.8287 (6)	0.3768 (3)	0.03447 (8)	0.0084 (4)
C4	−0.0157 (6)	0.4576 (3)	0.56123 (8)	0.0083 (4)
C5	0.1411 (6)	0.3397 (3)	0.51849 (8)	0.0080 (4)
C6	0.1634 (6)	0.3792 (3)	0.46131 (8)	0.0082 (4)
C7	0.4737 (6)	0.4533 (3)	0.21394 (9)	0.0105 (4)
H7	0.4338	0.5520	0.1918	0.013*
C8	0.3932 (6)	0.4577 (3)	0.27438 (9)	0.0100 (4)
H8	0.2997	0.5592	0.2914	0.012*
C9	0.5850 (6)	0.1841 (3)	0.28184 (8)	0.0077 (4)
C10	0.6588 (6)	0.0413 (3)	0.31613 (9)	0.0114 (4)
H10	0.6112	0.0446	0.3571	0.014*
C11	0.7991 (6)	−0.1021 (3)	0.29023 (9)	0.0129 (5)
H11	0.8500	−0.1977	0.3133	0.015*
C12	0.8687 (6)	−0.1080 (3)	0.22886 (9)	0.0132 (5)
H12	0.9628	−0.2085	0.2112	0.016*
C13	0.8022 (6)	0.0286 (3)	0.19491 (9)	0.0111 (4)
H13	0.8501	0.0228	0.1540	0.013*
C14	0.6621 (6)	0.1784 (3)	0.22068 (8)	0.0082 (4)
H2	0.669 (8)	0.311 (4)	0.1043 (12)	0.018 (7)*
H4	0.338 (14)	0.312 (7)	0.388 (2)	0.110 (19)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0151 (3)	0.0100 (3)	0.0103 (3)	−0.0034 (2)	0.00261 (18)	−0.00259 (17)
Cl2	0.0171 (3)	0.0093 (3)	0.0107 (3)	0.0050 (2)	0.00351 (18)	0.00301 (17)
O1	0.0168 (9)	0.0148 (9)	0.0057 (7)	−0.0014 (7)	0.0041 (6)	0.0002 (5)
O2	0.0203 (10)	0.0120 (9)	0.0047 (7)	−0.0050 (7)	0.0051 (6)	0.0007 (5)
O3	0.0185 (9)	0.0134 (9)	0.0063 (7)	0.0027 (7)	0.0049 (6)	0.0020 (5)
O4	0.0194 (9)	0.0112 (9)	0.0066 (7)	0.0054 (7)	0.0056 (6)	0.0000 (5)
N1	0.0077 (10)	0.0131 (10)	0.0068 (8)	−0.0019 (8)	0.0021 (6)	0.0004 (6)
N2	0.0097 (10)	0.0097 (10)	0.0073 (8)	0.0009 (7)	0.0024 (6)	−0.0003 (6)
C1	0.0052 (11)	0.0109 (11)	0.0063 (9)	0.0005 (8)	0.0009 (7)	0.0017 (7)
C2	0.0085 (11)	0.0069 (11)	0.0077 (9)	−0.0011 (8)	0.0017 (7)	0.0001 (7)
C3	0.0071 (11)	0.0095 (11)	0.0088 (10)	−0.0012 (9)	0.0011 (7)	0.0031 (7)
C4	0.0074 (11)	0.0096 (11)	0.0075 (9)	−0.0020 (8)	0.0011 (7)	−0.0008 (7)
C5	0.0095 (11)	0.0062 (11)	0.0085 (10)	0.0018 (8)	0.0002 (7)	0.0014 (7)
C6	0.0084 (11)	0.0083 (11)	0.0076 (10)	−0.0009 (8)	0.0024 (7)	−0.0018 (7)
C7	0.0086 (11)	0.0106 (11)	0.0126 (10)	−0.0008 (9)	0.0011 (8)	0.0025 (7)
C8	0.0100 (11)	0.0086 (11)	0.0115 (10)	0.0009 (9)	0.0022 (8)	−0.0003 (7)
C9	0.0071 (11)	0.0099 (11)	0.0060 (9)	−0.0011 (8)	0.0008 (7)	−0.0005 (7)
C10	0.0135 (12)	0.0113 (12)	0.0099 (10)	0.0016 (9)	0.0026 (7)	0.0016 (7)
C11	0.0133 (12)	0.0096 (12)	0.0161 (11)	0.0002 (9)	0.0013 (8)	0.0027 (8)
C12	0.0108 (12)	0.0114 (12)	0.0172 (11)	0.0008 (9)	0.0043 (8)	−0.0039 (8)
C13	0.0072 (11)	0.0140 (12)	0.0115 (10)	−0.0018 (9)	0.0028 (7)	−0.0034 (7)
C14	0.0053 (11)	0.0107 (12)	0.0084 (10)	−0.0019 (8)	0.0015 (7)	−0.0013 (7)

Geometric parameters (Å, °)

Cl1—C2	1.711 (2)	C4—C6^{ii}	1.508 (3)
Cl2—C5	1.713 (2)	C5—C6	1.348 (3)
O1—C1	1.232 (2)	C6—C4^{ii}	1.508 (3)
O2—C3	1.321 (2)	C7—C8	1.414 (3)
O2—H2	0.82 (3)	C7—H7	0.9500
O3—C4	1.221 (2)	C8—H8	0.9500
O4—C6	1.324 (2)	C9—C10	1.415 (3)
O4—H4	0.85 (5)	C9—C14	1.426 (3)
N1—C7	1.313 (3)	C10—C11	1.372 (3)
N1—C14	1.367 (3)	C10—H10	0.9500
N2—C8	1.316 (3)	C11—C12	1.423 (3)
N2—C9	1.368 (3)	C11—H11	0.9500
C1—C2	1.455 (3)	C12—C13	1.365 (3)
C1—C3^{i}	1.505 (3)	C12—H12	0.9500
C2—C3	1.356 (3)	C13—C14	1.411 (3)
C3—C1^{i}	1.505 (3)	C13—H13	0.9500
C4—C5	1.464 (3)		
C3—O2—H2	114 (2)	N1—C7—H7	118.9
C6—O4—H4	119 (4)	C8—C7—H7	118.9

C7—N1—C14	117.54 (16)	N2—C8—C7	122.4 (2)
C8—N2—C9	116.86 (17)	N2—C8—H8	118.8
O1—C1—C2	123.3 (2)	C7—C8—H8	118.8
O1—C1—C3^{i}	117.76 (19)	N2—C9—C10	119.65 (17)
C2—C1—C3^{i}	118.89 (17)	N2—C9—C14	120.90 (18)
C3—C2—C1	120.2 (2)	C10—C9—C14	119.45 (19)
C3—C2—Cl1	121.46 (17)	C11—C10—C9	119.96 (18)
C1—C2—Cl1	118.33 (15)	C11—C10—H10	120.0
O2—C3—C2	121.7 (2)	C9—C10—H10	120.0
O2—C3—C1^{i}	117.37 (17)	C10—C11—C12	120.2 (2)
C2—C3—C1^{i}	120.91 (19)	C10—C11—H11	119.9
O3—C4—C5	123.53 (19)	C12—C11—H11	119.9
O3—C4—C6^{ii}	118.54 (18)	C13—C12—C11	121.0 (2)
C5—C4—C6^{ii}	117.93 (17)	C13—C12—H12	119.5
C6—C5—C4	120.83 (19)	C11—C12—H12	119.5
C6—C5—Cl2	121.59 (17)	C12—C13—C14	119.89 (18)
C4—C5—Cl2	117.55 (14)	C12—C13—H13	120.1
O4—C6—C5	122.0 (2)	C14—C13—H13	120.1
O4—C6—C4^{ii}	116.79 (17)	N1—C14—C13	120.32 (17)
C5—C6—C4^{ii}	121.19 (18)	N1—C14—C9	120.20 (19)
N1—C7—C8	122.10 (19)	C13—C14—C9	119.48 (19)
O1—C1—C2—C3	179.6 (2)	C9—N2—C8—C7	1.3 (3)
C3^{i}—C1—C2—C3	0.1 (3)	N1—C7—C8—N2	0.4 (4)
O1—C1—C2—Cl1	−0.3 (3)	C8—N2—C9—C10	177.4 (2)
C3^{i}—C1—C2—Cl1	−179.79 (16)	C8—N2—C9—C14	−2.1 (3)
C1—C2—C3—O2	179.54 (18)	N2—C9—C10—C11	179.6 (2)
Cl1—C2—C3—O2	−0.6 (3)	C14—C9—C10—C11	−0.8 (3)
C1—C2—C3—C1^{i}	−0.1 (4)	C9—C10—C11—C12	−0.4 (4)
Cl1—C2—C3—C1^{i}	179.78 (16)	C10—C11—C12—C13	0.9 (4)
O3—C4—C5—C6	−177.5 (2)	C11—C12—C13—C14	0.0 (3)
C6^{ii}—C4—C5—C6	2.3 (4)	C7—N1—C14—C13	−179.5 (2)
O3—C4—C5—Cl2	0.8 (3)	C7—N1—C14—C9	0.3 (3)
C6^{ii}—C4—C5—Cl2	−179.44 (16)	C12—C13—C14—N1	178.6 (2)
C4—C5—C6—O4	177.7 (2)	C12—C13—C14—C9	−1.2 (3)
Cl2—C5—C6—O4	−0.5 (3)	N2—C9—C14—N1	1.3 (3)
C4—C5—C6—C4^{ii}	−2.3 (4)	C10—C9—C14—N1	−178.2 (2)
Cl2—C5—C6—C4^{ii}	179.43 (17)	N2—C9—C14—C13	−178.8 (2)
C14—N1—C7—C8	−1.1 (3)	C10—C9—C14—C13	1.6 (3)

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*; (ii) −*x*, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···N1	0.82 (3)	1.90 (3)	2.683 (2)	159 (3)
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C10—H10···Cl2^{iv}	0.95	2.78	3.560 (2)	140
C11—H11···O3^{iv}	0.95	2.59	3.538 (3)	173

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*; (ii) −*x*, −*y*+1, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*; (iv) −*x*+1, −*y*, −*z*+1.

Fig. 1

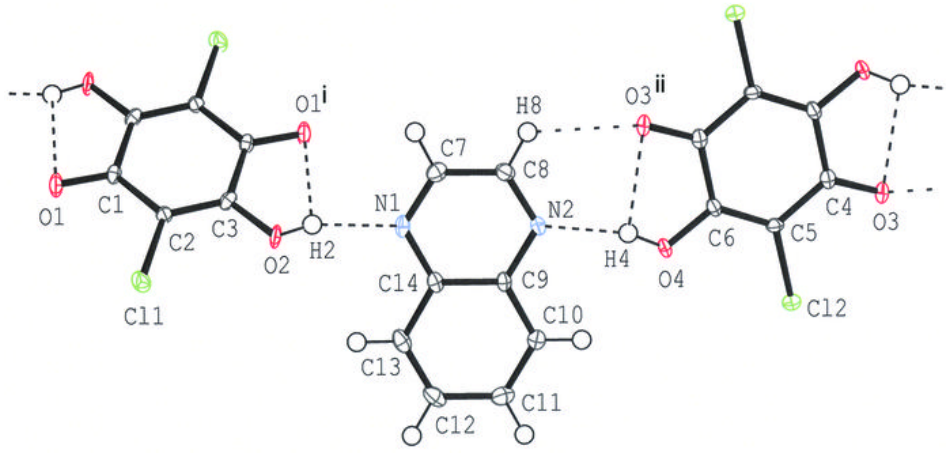
O1i
H8
O3ii
C7
C8
O1
C1
N1
N2
C4
O3
C2
C3
H2
H4
C6
C5
O2
O4
C14
C9
C10
C11
C13
C12
C12

Fig. 2