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Pyridine-3-carbonitrile–chloranilic acid–acetonitrile (2/1/2)

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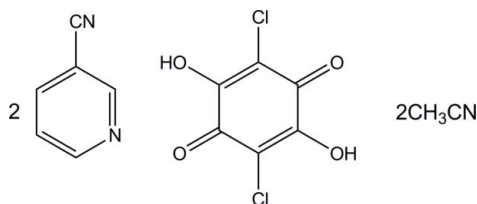
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 Key indicators: single-crystal X-ray study; $T = 180$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.035; wR factor = 0.099; data-to-parameter ratio = 20.3.

In the crystal structure of the title compound, $2\text{C}_6\text{H}_4\text{N}_2 \cdot \text{C}_6\text{H}_2\text{Cl}_2\text{O}_4 \cdot 2\text{C}_2\text{H}_3\text{N}$, the two symmetry-related pyridine-3-carbonitrile molecules are linked to either side of a chloranilic acid (systematic name: 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) molecule *via* intermolecular $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds, giving a centrosymmetric 2:1 unit. The dihedral angle between the pyridine ring and the chloranilic acid plane is $26.71(6)^\circ$. In addition, the two acetonitrile molecules are linked to either side of the 2:1 unit through $\text{C}-\text{H} \cdots \text{N}$ hydrogen bonds, forming a 2:1:2 aggregate. These 2:1:2 aggregates are further linked by weak intermolecular $\text{C}-\text{H} \cdots \text{N}$ and $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds, forming a tape along the c axis.

Related literature

For related structures, see, for example: Gotoh *et al.* (2009); Gotoh, Asaji & Ishida (2008); Gotoh, Nagoshi & Ishida (2008).



Experimental

Crystal data

 $2\text{C}_6\text{H}_4\text{N}_2 \cdot \text{C}_6\text{H}_2\text{Cl}_2\text{O}_4 \cdot 2\text{C}_2\text{H}_3\text{N}$
 $M_r = 499.31$

 Triclinic, $P\bar{1}$
 $a = 3.91269(16)$ Å

 $b = 10.8937(9)$ Å
 $c = 13.5966(5)$ Å
 $\alpha = 105.302(4)^\circ$
 $\beta = 90.0058(14)^\circ$
 $\gamma = 90.847(5)^\circ$
 $V = 558.93(6)$ Å³
 $Z = 1$

 Mo $K\alpha$ radiation

 $\mu = 0.33$ mm⁻¹
 $T = 180$ K

 $0.32 \times 0.25 \times 0.15$ mm

Data collection

 Rigaku RAXIS-RAPID II
 diffractometer
 Absorption correction: numerical
 (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.906$, $T_{\max} = 0.951$

 7721 measured reflections
 3232 independent reflections
 2592 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.099$
 $S = 1.07$
 3232 reflections
 159 parameters

 H atoms treated by a mixture of
 independent and constrained
 refinement
 $\Delta\rho_{\text{max}} = 0.44$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O}2-\text{H}2 \cdots \text{N}1$	0.92 (3)	1.75 (3)	2.6111 (17)	154 (3)
$\text{O}2-\text{H}2 \cdots \text{O}1^{\text{i}}$	0.92 (3)	2.25 (3)	2.6824 (14)	108 (2)
$\text{C}4-\text{H}4 \cdots \text{N}2^{\text{ii}}$	0.95	2.46	3.292 (2)	146
$\text{C}6-\text{H}6 \cdots \text{N}3$	0.95	2.57	3.385 (2)	144
$\text{C}7-\text{H}7 \cdots \text{O}1^{\text{iii}}$	0.95	2.48	3.4248 (18)	172
$\text{C}11-\text{H}11\text{A} \cdots \text{N}2$	0.98	2.62	3.341 (2)	130

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

Data collection: *PROCESS-AUTO* (Rigaku/MSK, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2901).

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supporting information

Acta Cryst. (2009). E65, o2467 [doi:10.1107/S1600536809036605]

Pyridine-3-carbonitrile–chloranilic acid–acetonitrile (2/1/2)

Kazuma Gotoh and Hiroyuki Ishida

S1. Comment

The title compound, (I), was prepared in order to extend our study on $D\cdots H\cdots A$ hydrogen bonding ($D = \text{N, O, or C}$; $A = \text{N, O or Cl}$) in amine–chloranilic acid systems (Gotoh, Asaji & Ishida, 2008; Gotoh *et al.*, 2009).

In the crystal structure of the title compound, two pyridine-3-carbonitrile molecules, one chloranilic acid molecule and two acetonitrile molecules are linked by $\text{O}\cdots\text{H}\cdots\text{N}$ and $\text{C}\cdots\text{H}\cdots\text{N}$ hydrogen bonds (Table 1) to afford a 2:1:2 aggregate (Fig. 1). The $\text{O}\cdots\text{N}$ distance [2.6111 (17) Å] between the acid and the base is comparable to that of 2.610 (3) Å in pyridine-4-carbonitrile–chloranilic acid (1/1), where the H atom in the $\text{O}\cdots\text{H}\cdots\text{N}$ hydrogen bond is disordered (Gotoh, Nagoshi & Ishida, 2008), but in the title compound no distinct evidence of H disorder was observed in a difference Fourier map. The 2:1:2 aggregates are linked by weak intermolecular $\text{C}\cdots\text{H}\cdots\text{N}$ and $\text{C}\cdots\text{H}\cdots\text{O}$ hydrogen bonds, forming a tape along the c axis (Fig. 2). A short contact between the adjacent $\text{C}\equiv\text{N}$ bonds of acetonitrile molecules is observed [$\text{C10}\cdots\text{C10}^{\text{iii}}$ 3.314 Å; symmetry code: (iii) $-x - 1, -y + 2, -z + 1$].

S2. Experimental

Single crystals were obtained by slow evaporation from an acetonitrile solution (120 ml) of chloranilic acid (250 mg) and pyridine-3-carbonitrile (250 mg) at room temperature.

S3. Refinement

C-bound H atoms were positioned geometrically ($\text{C}\cdots\text{H} = 0.95$ or 0.98 Å) and refined as riding, allowing for free rotation of the methyl group. $U_{\text{iso}}(\text{H})$ values were set at $1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$. The O-bound H atom was found in a difference Fourier map and refined isotropically. The refined $\text{O}\cdots\text{H}$ distance is 0.92 (3) Å.

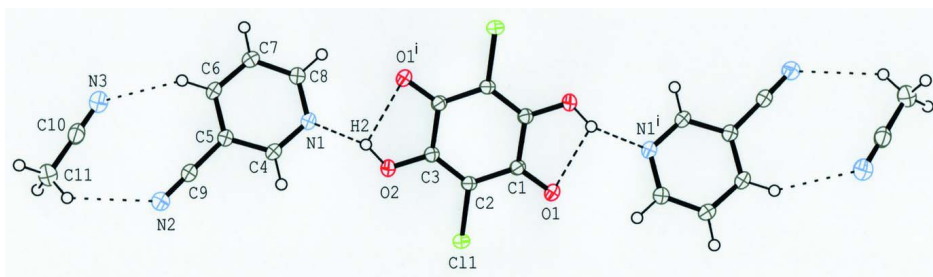
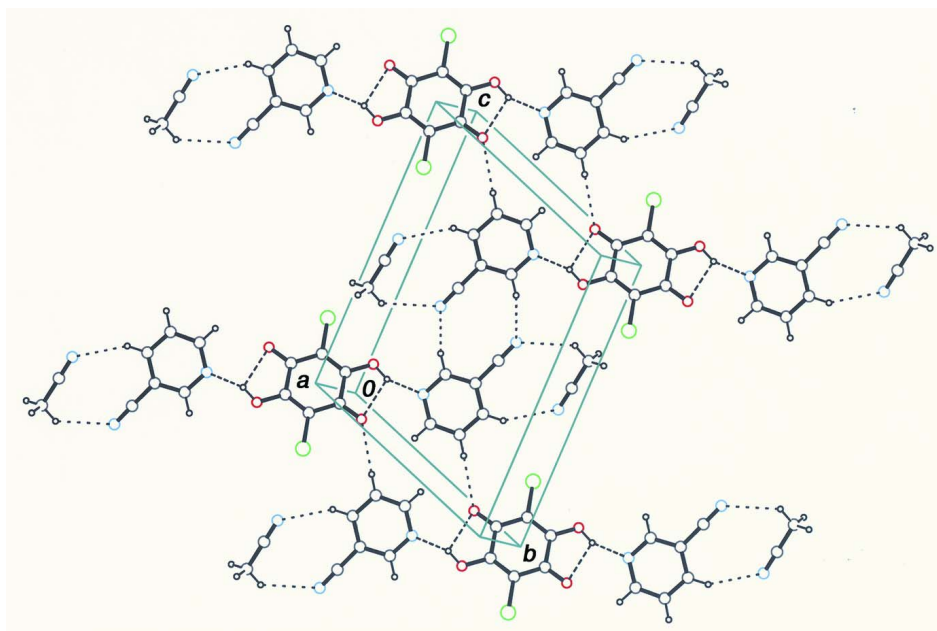


Figure 1

The molecular structure of the title compound, with the atom-labeling. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level. The dashed lines indicate $\text{O}\cdots\text{H}\cdots\text{O}$, $\text{O}\cdots\text{H}\cdots\text{N}$ and $\text{C}\cdots\text{H}\cdots\text{N}$ hydrogen bonds. [Symmetry code: (i) $-x + 2, -y, -z$].

**Figure 2**

A packing diagram of (I), showing a molecular tape running along the *c* axis. The dashed lines indicate O—H···O, O—H···N, C—H···N and C—H···O hydrogen bonds.

Pyridine-3-carbonitrile–chloranilic acid–acetonitrile (2/1/2)

Crystal data

$2\text{C}_6\text{H}_4\text{N}_2 \cdot \text{C}_6\text{H}_2\text{Cl}_2\text{O}_4 \cdot 2\text{C}_2\text{H}_3\text{N}$

$M_r = 499.31$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 3.91269\ (16)\ \text{\AA}$

$b = 10.8937\ (9)\ \text{\AA}$

$c = 13.5966\ (5)\ \text{\AA}$

$\alpha = 105.302\ (4)^\circ$

$\beta = 90.0058\ (14)^\circ$

$\gamma = 90.847\ (5)^\circ$

$V = 558.93\ (6)\ \text{\AA}^3$

$Z = 1$

$F(000) = 256.00$

$D_x = 1.483\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71075\ \text{\AA}$

Cell parameters from 6412 reflections

$\theta = 3.1\text{--}30.1^\circ$

$\mu = 0.33\ \text{mm}^{-1}$

$T = 180\ \text{K}$

Block, brown

$0.32 \times 0.25 \times 0.15\ \text{mm}$

Data collection

Rigaku RAXIS-RAPID II
diffractometer

Detector resolution: $10.00\ \text{pixels mm}^{-1}$

ω scans

Absorption correction: numerical
(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.906$, $T_{\max} = 0.951$

7721 measured reflections

3232 independent reflections

2592 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\text{max}} = 30.0^\circ$

$h = -5 \rightarrow 5$

$k = -15 \rightarrow 15$

$l = -19 \rightarrow 17$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.099$
 $S = 1.07$
 3232 reflections
 159 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 0.1506P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.74850 (9)	-0.11634 (3)	0.17747 (2)	0.02647 (10)
O1	1.1404 (3)	-0.24034 (9)	-0.00816 (7)	0.0278 (2)
O2	0.6357 (3)	0.14675 (10)	0.16065 (7)	0.0294 (2)
N1	0.4384 (3)	0.38133 (11)	0.18840 (9)	0.0268 (2)
N2	0.2005 (4)	0.63890 (12)	0.52232 (10)	0.0347 (3)
N3	-0.2867 (4)	0.85277 (13)	0.41743 (11)	0.0400 (3)
C1	1.0708 (3)	-0.12968 (12)	-0.00163 (9)	0.0213 (2)
C2	0.8789 (3)	-0.04984 (12)	0.08193 (9)	0.0208 (2)
C3	0.8076 (3)	0.07272 (12)	0.08605 (9)	0.0215 (2)
C4	0.3922 (4)	0.43073 (12)	0.28796 (10)	0.0254 (3)
H4	0.4423	0.3805	0.3335	0.031*
C5	0.2725 (3)	0.55390 (12)	0.32762 (10)	0.0233 (3)
C6	0.1973 (4)	0.62808 (13)	0.26185 (10)	0.0265 (3)
H6	0.1169	0.7124	0.2871	0.032*
C7	0.2431 (4)	0.57525 (13)	0.15812 (11)	0.0281 (3)
H7	0.1922	0.6227	0.1106	0.034*
C8	0.3640 (4)	0.45244 (13)	0.12482 (10)	0.0270 (3)
H8	0.3956	0.4171	0.0537	0.032*
C9	0.2324 (4)	0.60218 (13)	0.43620 (10)	0.0263 (3)
C10	-0.2753 (4)	0.87366 (14)	0.50394 (12)	0.0310 (3)
C11	-0.2586 (4)	0.90013 (16)	0.61421 (12)	0.0365 (3)
H11A	-0.0933	0.8436	0.6332	0.055*
H11B	-0.4846	0.8857	0.6406	0.055*
H11C	-0.1869	0.9889	0.6432	0.055*

H2	0.596 (7)	0.226 (3)	0.152 (2)	0.082 (9)*
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Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.03569 (18)	0.02348 (16)	0.02309 (16)	0.00415 (12)	0.00557 (12)	0.01100 (11)
O1	0.0404 (5)	0.0181 (4)	0.0255 (5)	0.0062 (4)	0.0045 (4)	0.0065 (4)
O2	0.0445 (6)	0.0199 (5)	0.0242 (5)	0.0089 (4)	0.0100 (4)	0.0058 (4)
N1	0.0349 (6)	0.0203 (5)	0.0252 (5)	0.0066 (4)	0.0041 (5)	0.0061 (4)
N2	0.0488 (8)	0.0284 (6)	0.0272 (6)	0.0078 (5)	0.0018 (5)	0.0075 (5)
N3	0.0512 (8)	0.0302 (7)	0.0380 (7)	0.0070 (6)	0.0065 (6)	0.0076 (5)
C1	0.0267 (6)	0.0180 (5)	0.0194 (5)	0.0010 (4)	-0.0019 (5)	0.0053 (4)
C2	0.0272 (6)	0.0186 (6)	0.0174 (5)	0.0009 (4)	0.0006 (5)	0.0060 (4)
C3	0.0268 (6)	0.0188 (6)	0.0188 (5)	0.0017 (4)	-0.0010 (5)	0.0045 (4)
C4	0.0321 (7)	0.0199 (6)	0.0254 (6)	0.0057 (5)	0.0015 (5)	0.0077 (5)
C5	0.0272 (6)	0.0199 (6)	0.0226 (6)	0.0024 (5)	0.0009 (5)	0.0049 (5)
C6	0.0327 (7)	0.0188 (6)	0.0286 (7)	0.0065 (5)	0.0026 (5)	0.0070 (5)
C7	0.0365 (7)	0.0238 (6)	0.0261 (6)	0.0066 (5)	0.0010 (5)	0.0100 (5)
C8	0.0348 (7)	0.0229 (6)	0.0235 (6)	0.0048 (5)	0.0036 (5)	0.0062 (5)
C9	0.0316 (7)	0.0205 (6)	0.0273 (6)	0.0052 (5)	0.0015 (5)	0.0067 (5)
C10	0.0307 (7)	0.0227 (6)	0.0387 (8)	0.0033 (5)	0.0063 (6)	0.0061 (5)
C11	0.0407 (8)	0.0335 (8)	0.0329 (8)	0.0040 (6)	0.0042 (6)	0.0044 (6)

Geometric parameters (Å, °)

C11—C2	1.7200 (13)	C4—H4	0.9500
O1—C1	1.2201 (15)	C5—C6	1.3884 (18)
O2—C3	1.3099 (15)	C5—C9	1.4399 (18)
O2—H2	0.91 (3)	C6—C7	1.3883 (19)
N1—C4	1.3316 (17)	C6—H6	0.9500
N1—C8	1.3387 (18)	C7—C8	1.3848 (19)
N2—C9	1.1406 (18)	C7—H7	0.9500
N3—C10	1.138 (2)	C8—H8	0.9500
C1—C2	1.4521 (17)	C10—C11	1.451 (2)
C1—C3 ⁱ	1.5153 (18)	C11—H11A	0.9800
C2—C3	1.3546 (17)	C11—H11B	0.9800
C3—C1 ⁱ	1.5153 (18)	C11—H11C	0.9800
C4—C5	1.3955 (18)		
C3—O2—H2	114.0 (17)	C7—C6—C5	117.96 (12)
C4—N1—C8	118.49 (11)	C7—C6—H6	121.0
O1—C1—C2	123.93 (12)	C5—C6—H6	121.0
O1—C1—C3 ⁱ	117.75 (11)	C8—C7—C6	119.07 (12)
C2—C1—C3 ⁱ	118.31 (10)	C8—C7—H7	120.5
C3—C2—C1	121.90 (11)	C6—C7—H7	120.5
C3—C2—C11	120.77 (10)	N1—C8—C7	122.88 (13)
C1—C2—C11	117.33 (9)	N1—C8—H8	118.6
O2—C3—C2	123.08 (12)	C7—C8—H8	118.6

O2—C3—C1 ⁱ	117.14 (11)	N2—C9—C5	179.14 (15)
C2—C3—C1 ⁱ	119.78 (11)	N3—C10—C11	179.69 (18)
N1—C4—C5	122.13 (12)	C10—C11—H11A	109.5
N1—C4—H4	118.9	C10—C11—H11B	109.5
C5—C4—H4	118.9	H11A—C11—H11B	109.5
C6—C5—C4	119.46 (12)	C10—C11—H11C	109.5
C6—C5—C9	121.20 (12)	H11A—C11—H11C	109.5
C4—C5—C9	119.34 (12)	H11B—C11—H11C	109.5
O1—C1—C2—C3	179.96 (13)	C8—N1—C4—C5	-0.6 (2)
C3 ⁱ —C1—C2—C3	-0.1 (2)	N1—C4—C5—C6	0.2 (2)
O1—C1—C2—C11	0.78 (18)	N1—C4—C5—C9	-179.19 (13)
C3 ⁱ —C1—C2—C11	-179.23 (9)	C4—C5—C6—C7	0.4 (2)
C1—C2—C3—O2	-179.86 (12)	C9—C5—C6—C7	179.82 (13)
C11—C2—C3—O2	-0.72 (19)	C5—C6—C7—C8	-0.6 (2)
C1—C2—C3—C1 ⁱ	0.1 (2)	C4—N1—C8—C7	0.4 (2)
C11—C2—C3—C1 ⁱ	179.21 (9)	C6—C7—C8—N1	0.3 (2)

Symmetry code: (i) $-x+2, -y, -z$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O2—H2...N1	0.92 (3)	1.75 (3)	2.6111 (17)	154 (3)
O2—H2...O1 ⁱ	0.92 (3)	2.25 (3)	2.6824 (14)	108 (2)
C4—H4...N2 ⁱⁱ	0.95	2.46	3.292 (2)	146
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