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## Structure Reports

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4-Chloro-2-nitrobenzoic acid–pyrazine  
(2/1)

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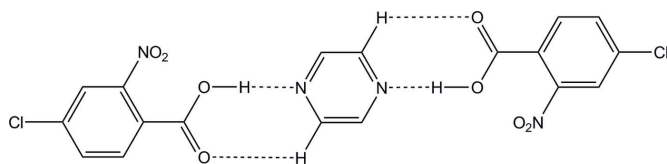
Received 17 October 2011; accepted 2 November 2011

Key indicators: single-crystal X-ray study;  $T = 110$  K; mean  $\sigma(\text{C}-\text{C}) = 0.001$  Å;  $R$  factor = 0.029;  $wR$  factor = 0.081; data-to-parameter ratio = 19.0.

In the title co-crystal,  $2\text{C}_7\text{H}_4\text{ClNO}_4 \cdot \text{C}_4\text{H}_4\text{N}_2$ , the pyrazine molecule is located on an inversion centre, so that the asymmetric unit consists of one molecule of 4-chloro-2-nitrobenzoic acid and a half-molecule of pyrazine. The components are connected by  $\text{O}-\text{H} \cdots \text{N}$  and  $\text{C}-\text{H} \cdots \text{O}$  hydrogen bonds, forming a 2:1 unit. In the hydrogen-bonded unit, the dihedral angle between the pyrazine ring and the benzene ring of the benzoic acid is  $16.55$  (4)°. The units are linked by intermolecular  $\text{C}-\text{H} \cdots \text{O}$  hydrogen bonds, forming a sheet structure parallel to  $(\bar{1}04)$ . A  $\text{C}-\text{H} \cdots \text{O}$  hydrogen-bond linkage is also observed between these sheets.

## Related literature

For related structures, see: Gotoh & Ishida (2009); Gotoh *et al.* (2010); Ishida *et al.* (2001).



## Experimental

## Crystal data

$2\text{C}_7\text{H}_4\text{ClNO}_4 \cdot \text{C}_4\text{H}_4\text{N}_2$   
 $M_r = 483.22$   
 Monoclinic,  $P2_1/c$   
 $a = 4.87662$  (13) Å

$b = 13.5385$  (3) Å  
 $c = 14.7981$  (6) Å  
 $\beta = 90.858$  (2)°  
 $V = 976.89$  (5) Å<sup>3</sup>

$Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.39$  mm<sup>-1</sup>

$T = 110$  K  
 $0.35 \times 0.15 \times 0.11$  mm

## Data collection

Rigaku R-Axis RAPID II diffractometer  
 Absorption correction: numerical (NUMABS; Higashi, 1999)  
 $T_{\min} = 0.904$ ,  $T_{\max} = 0.958$

19734 measured reflections  
 2833 independent reflections  
 2535 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.032$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.081$   
 $S = 1.07$   
 2833 reflections  
 149 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.51$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.39$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O}2-\text{H}2 \cdots \text{N}2$	0.88 (2)	1.80 (2)	2.6739 (10)	178 (2)
$\text{C}3-\text{H}3 \cdots \text{O}1^i$	0.95	2.51	3.4305 (12)	162
$\text{C}6-\text{H}6 \cdots \text{O}3^{\text{ii}}$	0.95	2.59	3.4865 (13)	157
$\text{C}8-\text{H}8 \cdots \text{O}1$	0.95	2.55	3.2201 (12)	128
$\text{C}9-\text{H}9 \cdots \text{O}3^{\text{iii}}$	0.95	2.45	3.1273 (12)	128

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

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, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* (Rigaku/MSC, 2004) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2468).

## References

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## supporting information

*Acta Cryst.* (2011). E67, o3222 [https://doi.org/10.1107/S1600536811046113]

## 4-Chloro-2-nitrobenzoic acid–pyrazine (2/1)

Kazuma Gotoh and Hiroyuki Ishida

## S1. Comment

The title compound was prepared in order to extend our study on  $D-H\cdots A$  hydrogen bonding ( $D = N, O, \text{ or } C$ ;  $A = N, O$  or Cl) in pyridine–substituted benzoic acid systems (Gotoh & Ishida, 2009; Gotoh *et al.*, 2010). The structures of the (1/2) compounds of pyrazine with 2-chloro-4-nitrobenzoic acid and 2-chloro-5-nitrobenzoic acid have been reported (Ishida *et al.*, 2001).

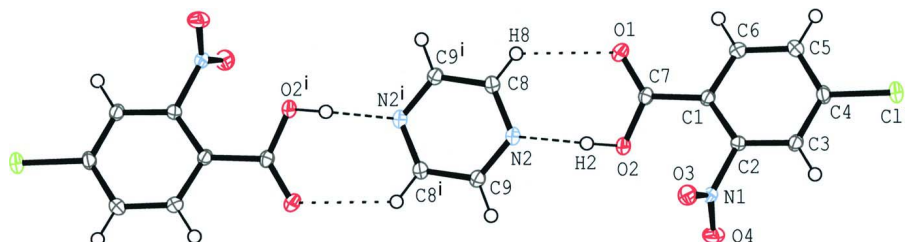
In the crystal structure of the title compound, no acid-base interaction involving proton transfer is observed between the two components, which are linked by  $O-H\cdots N$  and  $C-H\cdots O$  hydrogen bonds (Table 1 and Fig. 1). In the hydrogen-bonded 1:2 unit located on an inversion centre, the dihedral angle between the pyrazine ring and the benzene ring of the benzoic acid is  $16.55(4)^\circ$ . The carboxyl plane makes dihedral angles of  $7.15(11)$  and  $22.01(11)^\circ$ , respectively, with the pyrazine and benzene rings. The dihedral angle between the nitro group and the benzene ring is  $77.58(11)^\circ$ . The 1:2 units are linked by intermolecular  $C-H\cdots O$  hydrogen bonds between the acid molecules ( $C3-H3\cdots O1^{ii}$  and  $C6-H6\cdots O3^{iii}$ ; Table 1), forming a sheet parallel to the  $(\bar{1}04)$  plane (Fig. 2). The sheets are further linked by a  $C-H\cdots O$  hydrogen bond ( $C9-H9\cdots O^{iv}$ ; Table 1), forming a three-dimensional hydrogen-bonded network.

## S2. Experimental

Single crystals were obtained by slow evaporation from an acetonitrile solution (50 ml) of 4-chloro-2-nitrobenzoic acid (0.620 g) and pyrazine (0.123 g) at room temperature.

## S3. Refinement

C-bound H atoms were positioned geometrically ( $C-H = 0.95 \text{ \AA}$ ) and refined as riding, with  $U_{iso}(H) = 1.2U_{eq}(C)$ . The O-bound H atom was found in a difference Fourier map and refined freely. The refined  $O-H$  distance is  $0.88(2) \text{ \AA}$ .



**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 the  $O-H\cdots N$  and  $C-H\cdots O$  hydrogen bonds. [Symmetry code: (i)  $-x, -y + 1, -z$ .]

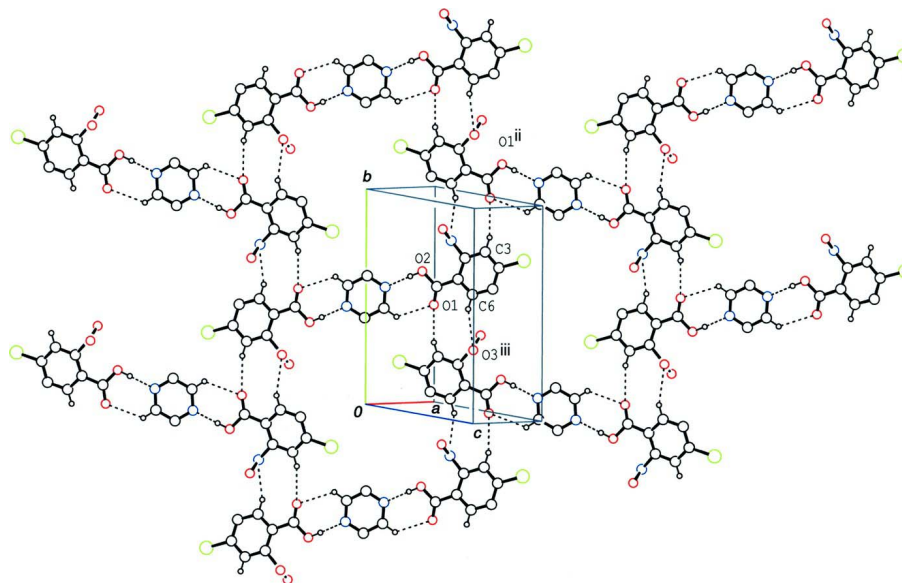


Figure 2

A packing diagram of the title compound, showing a sheet structure formed by O—H...N and C—H...O hydrogen bonds (dashed lines). [Symmetry codes: (ii)  $-x + 2, y + 1/2, -z + 1/2$ ; (iii)  $-x + 2, y - 1/2, -z + 1/2$ .]

#### 4-Chloro-2-nitrobenzoic acid–pyrazine (2/1)

##### Crystal data

$2C_7H_4ClNO_4 \cdot C_4H_4N_2$

$M_r = 483.22$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P 2_1/c$

$a = 4.87662 (13) \text{ \AA}$

$b = 13.5385 (3) \text{ \AA}$

$c = 14.7981 (6) \text{ \AA}$

$\beta = 90.858 (2)^\circ$

$V = 976.89 (5) \text{ \AA}^3$

$Z = 2$

$F(000) = 492.00$

$D_x = 1.643 \text{ Mg m}^{-3}$

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

Cell parameters from 16875 reflections

$\theta = 3.0\text{--}30.1^\circ$

$\mu = 0.39 \text{ mm}^{-1}$

$T = 110 \text{ K}$

Block, colorless

$0.35 \times 0.15 \times 0.11 \text{ mm}$

##### Data collection

Rigaku R-AXIS RAPID II  
diffractometer

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

$\omega$  scans

Absorption correction: numerical  
(*NUMABS*; Higashi, 1999)

$T_{\min} = 0.904, T_{\max} = 0.958$

19734 measured reflections

2833 independent reflections

2535 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

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

$h = -6 \rightarrow 6$

$k = -19 \rightarrow 19$

$l = -20 \rightarrow 20$

##### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.081$

$S = 1.07$

2833 reflections

149 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

$$w = 1/[\sigma^2(F_o^2) + (0.0499P)^2 + 0.2334P]$$

where  $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.51 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$$

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	1.52398 (5)	0.692432 (19)	0.490381 (17)	0.02257 (8)
O1	0.69354 (15)	0.47150 (5)	0.18863 (5)	0.02033 (15)
O2	0.54429 (14)	0.62747 (5)	0.17436 (5)	0.01875 (15)
O3	0.99168 (16)	0.77178 (6)	0.14572 (5)	0.02218 (16)
O4	0.72288 (16)	0.82806 (6)	0.25018 (5)	0.02337 (17)
N1	0.89159 (16)	0.76980 (6)	0.22167 (5)	0.01549 (16)
N2	0.18864 (16)	0.54745 (6)	0.05617 (5)	0.01577 (16)
C1	0.90441 (18)	0.59589 (7)	0.27806 (6)	0.01446 (17)
C2	0.99232 (19)	0.69339 (6)	0.28474 (6)	0.01377 (17)
C3	1.18351 (19)	0.72540 (7)	0.34825 (6)	0.01557 (18)
H3	1.2416	0.7923	0.3504	0.019*
C4	1.28706 (19)	0.65599 (7)	0.40871 (7)	0.01698 (18)
C5	1.2038 (2)	0.55818 (7)	0.40559 (7)	0.01984 (19)
H5	1.2757	0.5117	0.4478	0.024*
C6	1.0143 (2)	0.52883 (7)	0.34015 (7)	0.01845 (19)
H6	0.9584	0.4617	0.3376	0.022*
C7	0.70336 (18)	0.55797 (7)	0.20900 (6)	0.01475 (17)
C8	0.18281 (19)	0.44916 (7)	0.04969 (6)	0.01661 (18)
H8	0.3099	0.4109	0.0841	0.020*
C9	0.00621 (19)	0.59808 (7)	0.00657 (6)	0.01588 (18)
H9	0.0056	0.6682	0.0098	0.019*
H2	0.429 (4)	0.6024 (14)	0.1346 (14)	0.050 (5)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.02064 (13)	0.02541 (14)	0.02136 (13)	-0.00126 (9)	-0.00925 (9)	-0.00274 (9)
O1	0.0212 (3)	0.0153 (3)	0.0243 (4)	-0.0027 (3)	-0.0041 (3)	-0.0039 (3)
O2	0.0174 (3)	0.0171 (3)	0.0215 (4)	0.0001 (3)	-0.0072 (3)	-0.0038 (3)
O3	0.0290 (4)	0.0224 (4)	0.0151 (3)	-0.0004 (3)	0.0005 (3)	0.0007 (3)
O4	0.0249 (4)	0.0182 (3)	0.0271 (4)	0.0068 (3)	0.0004 (3)	-0.0010 (3)

N1	0.0167 (4)	0.0131 (3)	0.0166 (4)	-0.0019 (3)	-0.0031 (3)	-0.0010 (3)
N2	0.0148 (3)	0.0181 (4)	0.0144 (4)	-0.0023 (3)	-0.0012 (3)	-0.0013 (3)
C1	0.0139 (4)	0.0135 (4)	0.0160 (4)	-0.0009 (3)	-0.0011 (3)	-0.0025 (3)
C2	0.0138 (4)	0.0135 (4)	0.0139 (4)	0.0011 (3)	-0.0007 (3)	-0.0008 (3)
C3	0.0150 (4)	0.0150 (4)	0.0167 (4)	-0.0015 (3)	-0.0012 (3)	-0.0025 (3)
C4	0.0146 (4)	0.0199 (4)	0.0163 (4)	0.0005 (3)	-0.0037 (3)	-0.0024 (3)
C5	0.0207 (4)	0.0179 (4)	0.0208 (4)	0.0015 (4)	-0.0059 (4)	0.0014 (4)
C6	0.0200 (4)	0.0138 (4)	0.0215 (4)	-0.0005 (3)	-0.0036 (3)	-0.0002 (3)
C7	0.0131 (4)	0.0160 (4)	0.0151 (4)	-0.0022 (3)	0.0002 (3)	-0.0017 (3)
C8	0.0160 (4)	0.0178 (4)	0.0159 (4)	-0.0004 (3)	-0.0019 (3)	-0.0006 (3)
C9	0.0165 (4)	0.0154 (4)	0.0157 (4)	-0.0017 (3)	-0.0003 (3)	-0.0010 (3)

*Geometric parameters (Å, °)*

C11—C4	1.7313 (10)	C2—C3	1.3836 (12)
O1—C7	1.2095 (11)	C3—C4	1.3875 (13)
O2—C7	1.3183 (11)	C3—H3	0.9500
O2—H2	0.88 (2)	C4—C5	1.3855 (14)
O3—N1	1.2323 (11)	C5—C6	1.3866 (13)
O4—N1	1.2195 (11)	C5—H5	0.9500
N1—C2	1.4727 (12)	C6—H6	0.9500
N2—C9	1.3343 (12)	C8—C9 <sup>i</sup>	1.3888 (13)
N2—C8	1.3344 (13)	C8—H8	0.9500
C1—C2	1.3909 (12)	C9—C8 <sup>i</sup>	1.3888 (13)
C1—C6	1.3932 (13)	C9—H9	0.9500
C1—C7	1.4964 (12)		
C7—O2—H2	110.7 (12)	C3—C4—C11	119.32 (7)
O4—N1—O3	125.45 (9)	C4—C5—C6	119.28 (9)
O4—N1—C2	117.09 (8)	C4—C5—H5	120.4
O3—N1—C2	117.41 (8)	C6—C5—H5	120.4
C9—N2—C8	117.35 (8)	C5—C6—C1	121.31 (9)
C2—C1—C6	117.15 (8)	C5—C6—H6	119.3
C2—C1—C7	124.91 (8)	C1—C6—H6	119.3
C6—C1—C7	117.93 (8)	O1—C7—O2	124.96 (9)
C3—C2—C1	123.33 (8)	O1—C7—C1	121.69 (9)
C3—C2—N1	115.18 (8)	O2—C7—C1	113.35 (8)
C1—C2—N1	121.47 (8)	N2—C8—C9 <sup>i</sup>	121.03 (8)
C2—C3—C4	117.45 (9)	N2—C8—H8	119.5
C2—C3—H3	121.3	C9 <sup>i</sup> —C8—H8	119.5
C4—C3—H3	121.3	N2—C9—C8 <sup>i</sup>	121.62 (9)
C5—C4—C3	121.48 (9)	N2—C9—H9	119.2
C5—C4—C11	119.20 (7)	C8 <sup>i</sup> —C9—H9	119.2
C6—C1—C2—C3	1.03 (14)	C3—C4—C5—C6	0.51 (15)
C7—C1—C2—C3	-178.46 (9)	C11—C4—C5—C6	-179.92 (8)
C6—C1—C2—N1	179.18 (9)	C4—C5—C6—C1	-0.57 (15)
C7—C1—C2—N1	-0.31 (14)	C2—C1—C6—C5	-0.16 (15)

O4—N1—C2—C3	-77.08 (11)	C7—C1—C6—C5	179.36 (9)
O3—N1—C2—C3	100.39 (10)	C2—C1—C7—O1	157.90 (10)
O4—N1—C2—C1	104.62 (10)	C6—C1—C7—O1	-21.58 (14)
O3—N1—C2—C1	-77.91 (11)	C2—C1—C7—O2	-22.11 (13)
C1—C2—C3—C4	-1.09 (14)	C6—C1—C7—O2	158.41 (9)
N1—C2—C3—C4	-179.35 (8)	C9—N2—C8—C9 <sup>i</sup>	-0.01 (15)
C2—C3—C4—C5	0.29 (15)	C8—N2—C9—C8 <sup>i</sup>	0.01 (15)
C2—C3—C4—Cl1	-179.28 (7)		

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

#### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 $\cdots$ N2	0.88 (2)	1.80 (2)	2.6739 (10)	178 (2)
C3—H3 $\cdots$ O1 <sup>ii</sup>	0.95	2.51	3.4305 (12)	162
C6—H6 $\cdots$ O3 <sup>iii</sup>	0.95	2.59	3.4865 (13)	157
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C9—H9 $\cdots$ O3 <sup>iv</sup>	0.95	2.45	3.1273 (12)	128

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