Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

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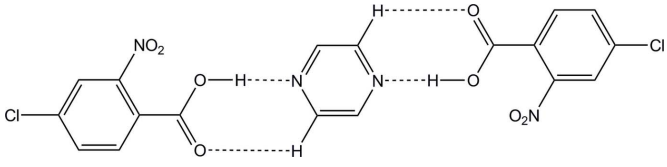
Received 17 October 2011; accepted 2 November 2011

Key indicators: single-crystal X-ray study; T = 110 K; mean σ(C–C) = 0.001 Å; R factor = 0.029; wR factor = 0.081; data-to-parameter ratio = 19.0.

In the title co-crystal, $2C_7H_4ClNO_4\cdot C_4H_4N_2$, 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 O—H···N and C—H···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 C—H···O hydrogen bonds, forming a sheet structure parallel to ($\bar{1}$04). A C—H···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

$2C_7H_4ClNO_4\cdot C_4H_4N_2$
M_r = 483.22
Monoclinic, $P2_1/c$
a = 4.87662 (13) Å
b = 13.5385 (3) Å
c = 14.7981 (6) Å
β = 90.858 (2)°
V = 976.89 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.39 mm^{-1}
T = 110 K
0.35 × 0.15 × 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_{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^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···N2	0.88 (2)	1.80 (2)	2.6739 (10)	178 (2)
C3—H3···O1^{i}	0.95	2.51	3.4305 (12)	162
C6—H6···O3^{ii}	0.95	2.59	3.4865 (13)	157
C8—H8···O1	0.95	2.55	3.2201 (12)	128
C9—H9···O3^{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).

This work was supported by a Grant-in-Aid for Scientific Research (C) (No. 22550013) from the Japan Society for the Promotion of Science.

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

References

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Gotoh, K. & Ishida, H. (2009). *Acta Cryst.* C**65**, o534–o538.
Gotoh, K., Katagiri, K. & Ishida, H. (2010). *Acta Cryst.* E**66**, o3190.
Higashi, T. (1999). *NUMABS*. Rigaku Corporation, Tokyo, Japan.
Ishida, H., Rahman, B. & Kashino, S. (2001). *Acta Cryst.* C**57**, 876–879.
Rigaku/MSC. (2004). *PROCESS-AUTO* and *CrystalStructure*. Rigaku/MSC Inc., The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2011). E**67**, o3222 [**doi:10.1107/S1600536811046113**]

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

K. Gotoh 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 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···N and C—H···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)°. The carboxyl plane makes dihedral angles of 7.15 (11) and 22.01 (11)°, respectively, with the pyrazine and benzene rings. The dihedral angle between the nitro group and the benzene ring is 77.58 (11)°. The 1:2 units are linked by intermolecular C—H···O hydrogen bonds between the acid molecules (C3—H3···O1^{ii} and C6—H6···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···O hydrogen bond (C9—H9···O^{iv}; Table 1), forming a three-dimensional hydrogen-bonded network.

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.

Refinement

C-bound H atoms were positioned geometrically (C—H = 0.95 Å) 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) Å.

Figures

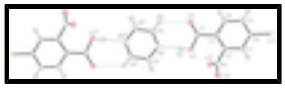


Fig. 1. The molecular structure of the title compound, with the atom-labeling. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level. The dashed lines indicate the O—H···N and C—H···O hydrogen bonds. [Symmetry code: (i) -*x*, -*y* + 1, -*z*.]

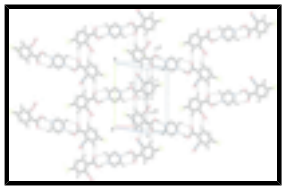


Fig. 2. A packing diagram of the title compound, showing a sheet structure formed by O—H···N and C—H···O hydrogen bonds (dashed lines). [Symmetry codes: (ii) -*x* + 2, *y* + 1/2, -*z* + 1/2; (iii) -*x* + 2, *y* - 1/2, -*z* + 1/2.]

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

Crystal data

$2C_7H_4ClNO_4 \cdot C_4H_4N_2$	$F(000) = 492.00$
$M_r = 483.22$	$D_x = 1.643$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Hall symbol: -P 2ybc	Cell parameters from 16875 reflections
$a = 4.87662$ (13) Å	$\theta = 3.0$–$30.1°$
$b = 13.5385$ (3) Å	$\mu = 0.39$ mm^{-1}
$c = 14.7981$ (6) Å	$T = 110$ K
$\beta = 90.858$ (2)°	Block, colorless
$V = 976.89$ (5) Å^3	0.35 × 0.15 × 0.11 mm
$Z = 2$	

Data collection

Rigaku R-AXIS RAPID II diffractometer	2535 reflections with $I > 2\sigma(I)$
Detector resolution: 10.00 pixels mm^{-1}	$R_{int} = 0.032$
ω scans	$\theta_{max} = 30.0°$
Absorption correction: numerical (*NUMABS*; Higashi, 1999)	$h = -6 \rightarrow 6$
$T_{min} = 0.904$, $T_{max} = 0.958$	$k = -19 \rightarrow 19$
19734 measured reflections	$l = -20 \rightarrow 20$
2833 independent reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.029$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.081$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.0499P)^2 + 0.2334P]$ where $P = (F_o^2 + 2F_c^2)/3$
2833 reflections	$(\Delta/\sigma)_{max} = 0.001$
149 parameters	$\Delta\rho_{max} = 0.51$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.39$ e Å^{-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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{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 (Å^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, °)

Cl1—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^{i}	1.3888 (13)
N2—C8	1.3344 (13)	C8—H8	0.9500
C1—C2	1.3909 (12)	C9—C8^{i}	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—Cl1	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^{i}	121.03 (8)
C2—C3—C4	117.45 (9)	N2—C8—H8	119.5
C2—C3—H3	121.3	C9^{i}—C8—H8	119.5
C4—C3—H3	121.3	N2—C9—C8^{i}	121.62 (9)
C5—C4—C3	121.48 (9)	N2—C9—H9	119.2
C5—C4—Cl1	119.20 (7)	C8^{i}—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)	Cl1—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^{i}	−0.01 (15)
C2—C3—C4—C5	0.29 (15)	C8—N2—C9—C8^{i}	0.01 (15)

C2—C3—C4—Cl1	−179.28 (7)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···N2	0.88 (2)	1.80 (2)	2.6739 (10)	178 (2)
C3—H3···O1^{ii}	0.95	2.51	3.4305 (12)	162
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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*.

Fig. 1

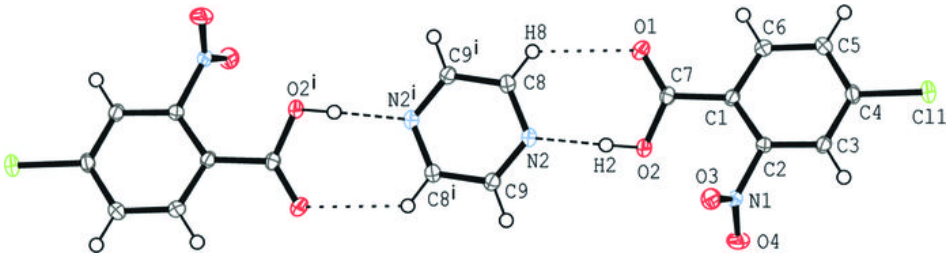

Fig. 2