

2:1 Complexes of 2-chloro-4-nitrobenzoic acid and 2-chloro-5-nitrobenzoic acid with pyrazine

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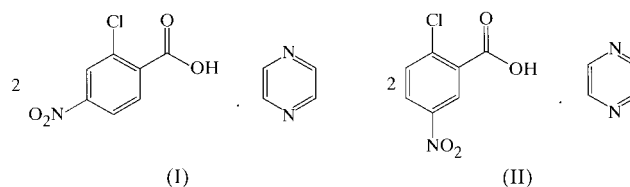
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2-Chloro-4-nitrobenzoic acid and 2-chloro-5-nitrobenzoic acid form $O-H\cdots N$ hydrogen bonds with pyrazine to afford 2:1 complexes of $2C_7H_4ClNO_4\cdot C_4H_4N_2$, (I) and (II), respectively, that are located on inversion centers. The $2C_7H_4ClNO_4\cdots C_4H_4N_2$ units in both complexes are connected by weak $C-H\cdots O$ hydrogen bonds; the units build a three-dimensional hydrogen-bond network in (I) and a ribbon structure in (II).

Comment

Several hydrogen-bonded complexes composed of 2-chloro-4-nitrobenzoic acid and amines were studied by Habeeb *et al.* using ^{35}Cl NQR and IR techniques (Kalenik *et al.*, 1989; Habeeb & Awad, 1995; Awad & Habeeb, 1996). They reported that the hydrogen bonds formed between the benzoic acid and the amines vary from an $O-H\cdots N$ to an $O\cdots H-N$ type with increasing proton affinities (PA) of the amines and that the critical (inversion) point at 50% proton transfer exists in the complex of 3,5-dimethylpyridine. However, there is not yet any crystallographic evidence supporting these findings. Moreover, the shapes of the proton donor and acceptor molecules may be as important as the PA in determining the proton transfer. This prompted us to carry out studies on the structure of chloro- and nitro-substituted benzoic acid-amine complexes. In addition to the $O-H\cdots N/O\cdots H-N$ hydrogen bond, other weak intermolecular interactions, such as $C-H\cdots O$ and $C-H\cdots Cl$ interactions, may be expected in these complexes, because the nitro group and the Cl atom of these benzoic acids can act as a weak hydrogen-bond acceptor (Robinson *et al.*, 2000; Desiraju & Steiner, 1999). It is of relevance, therefore, in the context of crystal engineering and supramolecular architecture to investigate the role of the weak hydrogen-bond acceptors in the crystal packing of the title complexes. In the present study, we took pyrazine as an amine having a quite small PA value and prepared the 2-chloro-4-nitrobenzoic acid-pyrazine (2/1) and 2-chloro-5-nitrobenzoic acid-pyrazine (2/1) complexes; their crystal structures were determined at room temperature. To our

knowledge, this is the first crystallographic report of 2-chloro-4-nitrobenzoic acid-amine and 2-chloro-5-nitrobenzoic acid-amine systems; no structural data of compounds composed of 2-chloro-4-nitrobenzoic acid and 2-chloro-5-nitrobenzoic acid, except 2-chloro-5-nitrobenzoic acid itself, are recorded in the Cambridge Structural Database (Version 5.20, October 2000; Allen & Kennard, 1993).



The pyrazine molecule in both the 2-chloro-4-nitrobenzoic acid-pyrazine (2/1) complex, (I), and the 2-chloro-5-nitrobenzoic acid-pyrazine (2/1) complex, (II), occupies a center of symmetry, and the asymmetric units of (I) and (II) are composed of $C_7H_4ClNO_4\cdot 0.5C_4H_4N_2$. In both crystals, the two components are held together by a short $O-H\cdots N$ hydrogen bond (Tables 2 and 4), forming the $2C_7H_4ClNO_4\cdot C_4H_4N_2$ unit (Figs. 1 and 2). No acid-base interaction involving a proton transfer is observed as expected from the small PA value of pyrazine. The $O\cdots N$ distances are long compared with the shortest expected $O\cdots N$ distance of *ca* 2.45 Å (Jerzykiewicz *et al.*, 1998), which may be realised in the vicinity of the critical point.

In (I), the dihedral angle between the nitro group and the benzene ring is $18.97(13)^\circ$ and that between the carboxyl group and the benzene ring is $32.77(12)^\circ$. The dihedral angle between the planes of the pyrazine and benzene rings is $19.56(12)^\circ$. On the other hand, in (II), all the atoms are located almost on a plane; the benzene ring makes small angles of $3.19(13)$, $9.17(13)$ and $5.56(13)^\circ$ with the nitro

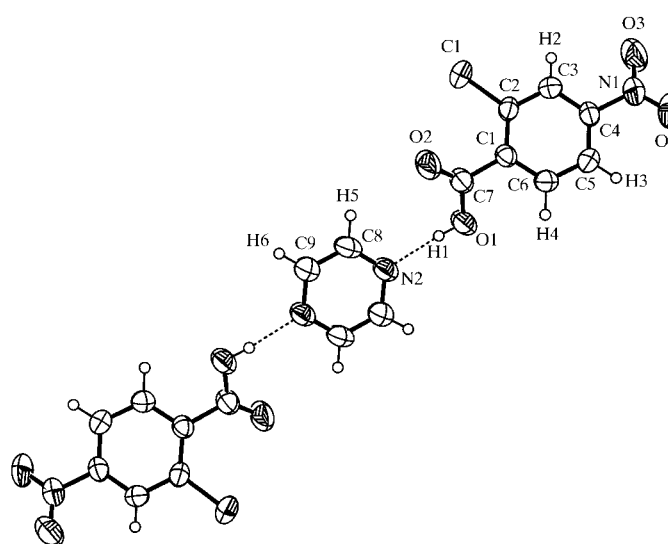


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of (I) showing the atomic labelling. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are drawn as circles of arbitrary size. Hydrogen bonds are indicated by dashed lines.

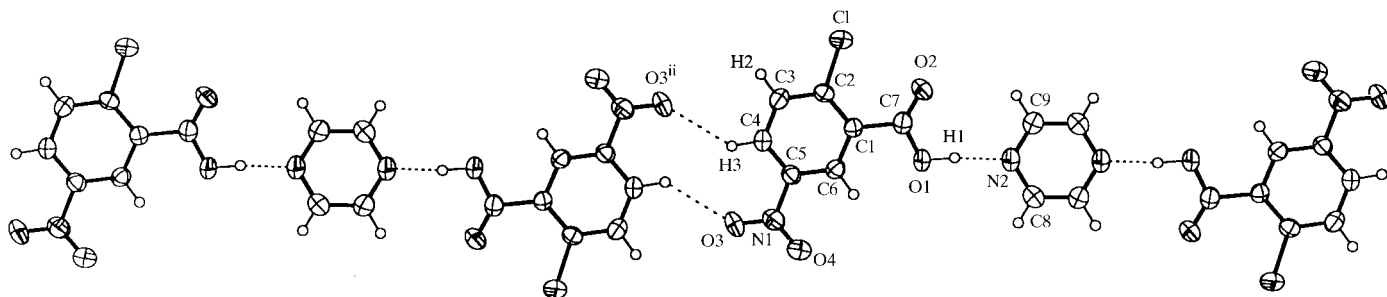


Figure 2

ORTEP-3 (Farrugia, 1997) drawing of a molecular ribbon of (II) showing the atomic labelling and hydrogen-bonding scheme. 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 codes are as in Table 4).

group, the carboxyl group and the pyrazine ring, respectively. To compare these geometries with those of the isolated molecules in the gas phase, we carried out *ab initio* molecular orbital calculations at the HF/6-31G** level of theory by using the computer program GAUSSIAN98 (Frisch *et al.*, 1998). The optimized geometries were confirmed to correspond to a potential energy minimum from vibrational analysis. The calculated dihedral angles of the nitro and carboxyl groups with the benzene ring are 0.3 and 30.1°, respectively, for 2-chloro-4-nitrobenzoic acid, and 0.5 and 20.0° for 2-chloro-5-nitrobenzoic acid. We also obtained flat structures for both benzoic acids, which were found not as a stable form but at a saddle point of first order. The angles of the nitro group in (I) and the carboxyl group in (II) are much larger and smaller, respectively, compared with calculated values, the former and the latter of which may be interpreted as arising from intermolecular C—H...O interactions involving the nitro groups and aromatic π - π stacking interactions, respectively, as mentioned below.

In (I), an intermolecular C—H...O interaction (Table 2) is observed between the benzene ring and the nitro group, forming a centrosymmetric ring with graph-set descriptor $R_2^2(10)$ (Bernstein *et al.*, 1995). The interaction connects the units of $2C_7H_4ClNO_4 \cdot C_4H_4N_2$ to build a zigzag chain running along the $[10\bar{1}]$ direction. The chains are linked by a C—H...O hydrogen bond formed between the benzene ring and the carboxyl group and a C—H...O interaction between the

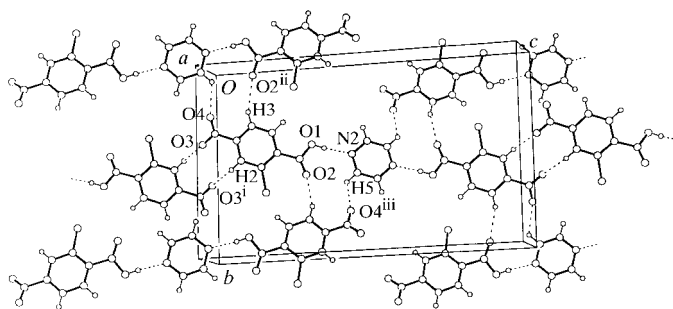


Figure 3

Part of the crystal structure of (I) showing the three-dimensional hydrogen-bond network formed via N—H...O and C—H...O hydrogen bonds, indicated by dashed lines (symmetry codes are as in Table 2).

pyrazine ring and the nitro group (Table 2), generating a three-dimensional hydrogen-bond network (Fig. 3).

In (II), a C—H...O interaction (Table 4) between the benzoic acids related by an inversion center forms the $R_2^2(10)$ ring with a similar geometry to that in (I) and links the $2C_7H_4ClNO_4 \cdot C_4H_4N_2$ units, resulting in the formation of ribbons running parallel to the $[210]$ and $[2\bar{1}0]$ directions. An additional weak C—H...O interaction (Table 4) and a

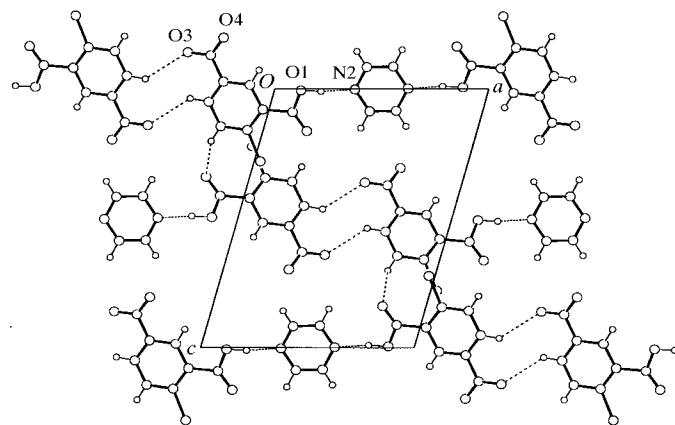


Figure 4

Part of the crystal structure of (II) showing the formation of the molecular layers built from flat ribbons. Hydrogen bonds are indicated by dashed lines.

Cl...Clⁱ contact at 3.7378 (12) Å [symmetry code: (i) $-x, \frac{1}{2} + y, \frac{1}{2} - z$] are found between the ribbons running in different directions. The ribbons are stacked along the *b* axis, forming two kinds of layers (Fig. 4), in which the benzoic acids related by an inversion center are stacked through π - π interactions with an interplanar spacing of 3.397 (5) Å and a centroid offset of 2.57 Å.

Experimental

Prismatic crystals of (I) and (II) were obtained by slow evaporation from benzene solutions of pyrazine with 2-chloro-4-nitrobenzoic acid or 2-chloro-5-nitrobenzoic acid (molar ratio 2:1), respectively, at room temperature.

Compound (I)

Crystal data

2C₇H₄ClNO₄·C₄H₄N₂
M_r = 483.22
 Monoclinic, *P*2₁/*n*
a = 3.8280 (5) Å
b = 12.7738 (16) Å
c = 21.203 (3) Å
 β = 91.118 (14)°
V = 1036.6 (2) Å³
Z = 2

D_x = 1.548 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 11.1–12.4°
 μ = 0.37 mm⁻¹
T = 296 K
 Prismatic, colorless
 0.40 × 0.30 × 0.30 mm

Data collection

Rigaku AFC-5R diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
T_{min} = 0.862, *T_{max}* = 0.895
 3559 measured reflections
 2477 independent reflections
 1275 reflections with *I* > 2.0σ(*I*)

R_{int} = 0.031
 θ_{max} = 27.5°
h = -1 → 4
k = 0 → 16
l = -27 → 27
 3 standard reflections every 97 reflections
 intensity decay: 1.6%

Refinement

Refinement on *F*²
R(*F*) = 0.057
wR(*F*) = 0.063
S = 1.38
 2360 reflections
 169 parameters

All H-atom parameters refined
w = 1/[σ²(*F_o*) + 0.00003|*F_o*|²]
 (Δ/σ)_{max} = 0.01
 Δρ_{max} = 0.39 e Å⁻³
 Δρ_{min} = -0.49 e Å⁻³

Table 1

Selected bond lengths (Å) for (I).

Cl—C2	1.727 (2)	C1—C2	1.392 (3)
O1—C7	1.319 (3)	C1—C6	1.388 (3)
O2—C7	1.191 (3)	C1—C7	1.502 (3)
O3—N1	1.203 (3)	C2—C3	1.383 (3)
O4—N1	1.204 (3)	C3—C4	1.376 (3)
N1—C4	1.476 (3)	C4—C5	1.375 (3)
N2—C8	1.315 (3)	C5—C6	1.380 (3)
N2—C9 ⁱ	1.327 (3)	C8—C9	1.370 (4)

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

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...N2	0.84 (3)	1.85 (3)	2.686 (3)	175 (3)
C3—H2...O3 ⁱ	0.896 (19)	2.55 (2)	3.294 (4)	140.9 (18)
C5—H3...O2 ⁱⁱ	0.95 (2)	2.45 (2)	3.345 (3)	158 (2)
C8—H5...O4 ⁱⁱⁱ	0.93 (3)	2.48 (3)	3.053 (4)	120 (2)

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

Compound (II)

Crystal data

2C₇H₄ClNO₄·C₄H₄N₂
M_r = 483.22
 Monoclinic, *P*2₁/*c*
a = 10.293 (4) Å
b = 7.276 (2) Å
c = 13.818 (6) Å
 β = 105.17 (3)°
V = 998.9 (6) Å³
Z = 2

D_x = 1.606 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 10.0–12.5°
 μ = 0.38 mm⁻¹
T = 293 K
 Prismatic, colorless
 0.40 × 0.30 × 0.20 mm

Data collection

Rigaku AFC-5R diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
T_{min} = 0.810, *T_{max}* = 0.926
 2887 measured reflections
 2293 independent reflections
 1268 reflections with *I* > 2σ(*I*)

R_{int} = 0.039
 θ_{max} = 27.5°
h = -1 → 13
k = 0 → 9
l = -17 → 17
 3 standard reflections every 97 reflections
 intensity decay: 1.6%

Refinement

Refinement on *F*²
R(*F*) = 0.051
wR(*F*) = 0.061
S = 1.33
 2292 reflections
 170 parameters
 All H-atom parameters refined
w = 1/[σ²(*F_o*) + 0.00001|*F_o*|²]

(Δ/σ)_{max} = 0.01
 Δρ_{max} = 0.44 e Å⁻³
 Δρ_{min} = -0.61 e Å⁻³
 Extinction correction: Zachariasen (1967)
 Extinction coefficient: 2.48 (9) × 10⁻⁶

Table 3

Selected bond lengths (Å) for (II).

Cl—C2	1.730 (3)	C1—C2	1.401 (3)
O1—C7	1.308 (3)	C1—C6	1.396 (3)
O2—C7	1.197 (3)	C1—C7	1.512 (3)
O3—N1	1.218 (3)	C2—C3	1.387 (4)
O4—N1	1.216 (3)	C3—C4	1.377 (4)
N1—C5	1.481 (3)	C4—C5	1.370 (4)
N2—C8	1.335 (3)	C5—C6	1.375 (3)
N2—C9	1.327 (4)	C8—C9 ⁱ	1.376 (4)

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

Table 4

Hydrogen-bonding geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...N2	1.00 (3)	1.71 (3)	2.699 (3)	173 (3)
C3—H2...O2 ⁱ	0.96 (2)	2.64 (2)	3.496 (4)	149.3 (19)
C4—H3...O3 ⁱⁱ	0.97 (2)	2.53 (2)	3.301 (4)	136.8 (17)

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

H atoms were found in a difference Fourier map and refined isotropically. Refined distances: C—H = 0.90 (2)–0.99 (2) Å and O—H = 0.84 (3) Å for (I), and C—H = 0.95 (2)–1.00 (3) Å and O—H = 1.00 (3) Å for (II).

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1990); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993) for compound (I) and *SAPI90* (Fan, 1990) for compound (II); program(s) used to refine structure: *TEXSAN for Windows*; software used to prepare material for publication: *TEXSAN for Windows*.

X-ray measurements were made at the Okayama University X-ray Laboratory, Japan.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1601). Services for accessing these data are described at the back of the journal.

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