

Morpholinium 2-chloro-4-nitrobenzoate, 2-chloro-5-nitrobenzoate and 4-chloro-3-nitrobenzoate

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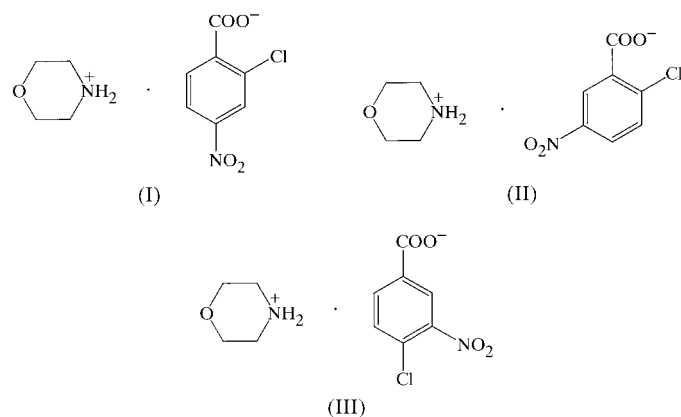
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Morpholinium 2-chloro-4-nitrobenzoate, $C_4H_{10}NO^+ \cdot C_7H_3ClNO_4^-$, (I), crystallizes in a non-centrosymmetric space group. The cations and anions are connected by $N-H \cdots O$ hydrogen bonds to afford a 2_1 helical chain. Morpholinium 2-chloro-5-nitrobenzoate, $C_4H_{10}NO^+ \cdot C_7H_3ClNO_4^-$, (II), and morpholinium 4-chloro-3-nitrobenzoate, $C_4H_{10}NO^+ \cdot C_7H_3ClNO_4^-$, (III), both crystallize in a centrosymmetric space group. In (II) and (III), two cations and two anions are held together by $N-H \cdots O$ hydrogen bonds to form a centrosymmetric ring with graph-set descriptor $R_4^4(12)$.

Comment

Chiral crystals composed of two achiral molecules have attracted much interest because of their potential use in absolute asymmetric synthesis (Green *et al.*, 1979; Koshima, Ding *et al.*, 1996; Tanaka & Toda, 2000) and non-linear optics (Koshima, Wang *et al.*, 1996). In the course of our study on $D-H \cdots A$ hydrogen bonding (D : N, O or C; A : N, O or Cl) in



chloro- and nitro-substituted benzoic acid–amine systems (Ishida *et al.*, 2001*a,b,c,d*), we found that imidazolium 2-chloro-4-nitrobenzoate crystallizes in the non-centrosymmetric space group $P2_1$. In the crystal, the cations and anions

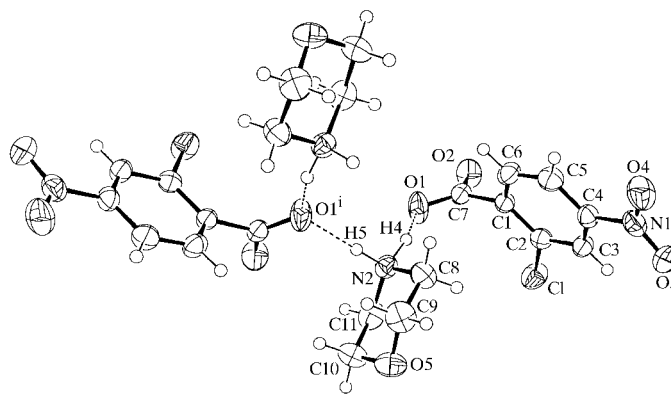


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of (I) with the atom-labeling scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. $N-H \cdots O$ hydrogen bonds are indicated by dashed lines [symmetry code: (i) $\frac{3}{2} - x, 1 - y, z - \frac{1}{2}$].

are connected by $N-H \cdots O$ hydrogen bonds to afford a 2_1 helical chain (Ishida *et al.*, 2001*d*). This is the first example of a chloro- and nitro-substituted benzoic acid–amine system that shows spontaneous resolution of a chiral rotational isomer of the benzoate ion. Thus, we have prepared crystals composed of chloro- and nitro-substituted benzoic acid and amine with the expectation that such a chiral rotational isomer exists

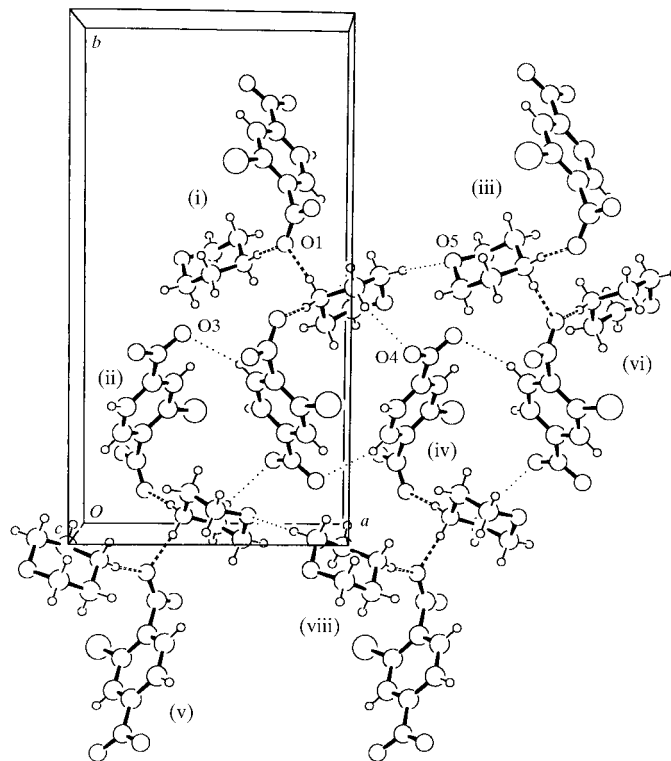


Figure 2
Packing diagram of (I) showing the helical structure formed *via* $N-H \cdots O$ hydrogen bonds, which are indicated by dashed lines. $C-H \cdots O$ interactions which connect the helical chains are indicated by dotted lines [symmetry codes: (i)–(iv) are as in Table 2; (v) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (vi) $1 + x, y, z$; (vii) $2 - x, y - \frac{1}{2}, \frac{3}{2} - z$].

widely in these systems; we have chosen morpholine as the counter-cation and prepared salts with 2-chloro-4-nitro-, (I), 2-chloro-5-nitro-, (II), and 4-chloro-3-nitrobenzoic acid, (III), and determined their crystal structures. Of these salts, (I) crystallizes in the non-centrosymmetric space group $P2_12_12_1$.

The asymmetric units of (I), (II) and (III) have the formula $C_4H_{10}NO^+ \cdot C_7H_3ClNO_4^-$. In these crystals, an acid–base interaction involving a proton transfer is observed, as expected from the high basicity of the amine present. In (I), the cations and anions are held together by short $N-H \cdots O$ hydrogen bonds (Table 2), forming a 2_1 helical chain along the c axis (Figs. 1 and 2). One of the O atoms of the carboxylate group, O1, forms two hydrogen bonds with the cations, while the other O atom, O2, forms no hydrogen bond. The C–O bond involved in the hydrogen bond is rather long [C7–O1 1.267 (3) Å] compared with the other C–O bond length [C7–O2 1.223 (4) Å] and the C–O bond lengths in (II) and (III) [1.237 (3)–1.247 (3) Å], where both O atoms of the carboxylate groups are involved in $N-H \cdots O$ hydrogen bonds (see below). The helical chains are linked by three main C–H \cdots O interactions (Table 2) involving both O atoms of the nitro group and the O atom of the cation (Fig. 2). The

carboxylate group is considerably twisted out of the plane of the benzene ring [dihedral angle 72.1 (2)°] compared with the calculated value (41.1°) for the isolated anion in the gas phase, using the *GAUSSIAN98/HF* program (Frisch *et al.*, 1998) with the 6-31G** basis set. On the other hand, the nitro group makes a small angle of 1.8 (2)° with the benzene ring, which is comparable to the calculated angle of 0.5°.

In (II) and (III), two cations and two anions are held together by short $N-H \cdots O$ hydrogen bonds (Tables 4 and 6). Both O atoms of the carboxylate groups are involved in the hydrogen bonds, forming centrosymmetric hydrogen-bonded rings (Figs. 3 and 4) with graph-set descriptor $R_4^4(12)$ (Bernstein *et al.*, 1995) in a similar manner to those observed in morpholinium 4-chloro-2-nitrobenzoate and 5-chloro-2-nitrobenzoate (Ishida *et al.*, 2001*b,c*). In (II), the dihedral angle between the carboxylate group and the benzene ring is 61.0 (2)° and that between the nitro group and the benzene ring is 11.7 (2)°. In (III), these dihedral angles are 13.2 (2)° and 19.3 (2)°, respectively. There are two and three important C–H \cdots O interactions in (II) and (III), respectively, which connect the macro-rings (Tables 4 and 6).

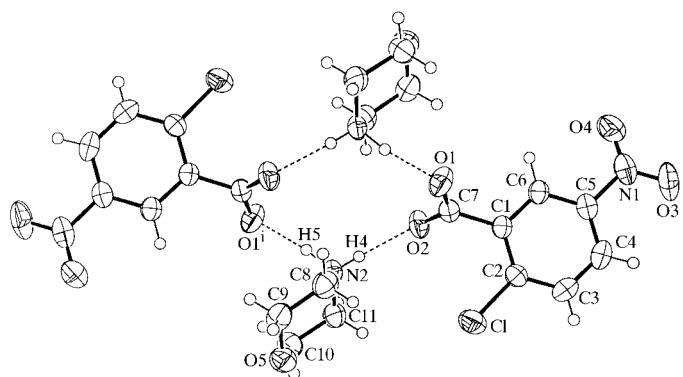


Figure 3
ORTEP-3 drawing of (II) showing a hydrogen-bonded ring. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. $N-H \cdots O$ hydrogen bonds are indicated by dashed lines [symmetry code: (i) $1 - x, -y, 1 - z$].

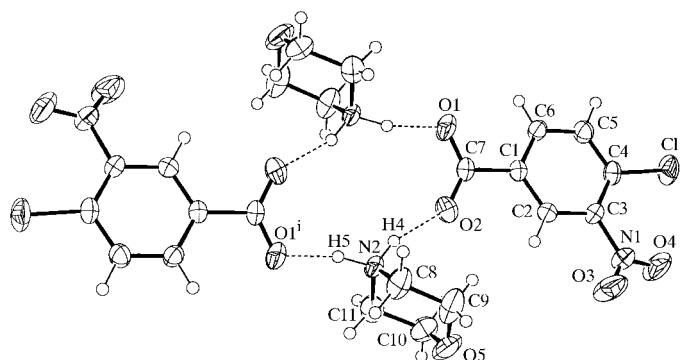


Figure 4
ORTEP-3 drawing of (III) showing a hydrogen-bonded ring. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. $N-H \cdots O$ hydrogen bonds are indicated by dashed lines [symmetry code: (i) $\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$].

Experimental

The title compounds were prepared by mixing morpholine with the corresponding benzoic acid (molar ratio of 1:1) in acetonitrile. Single crystals were grown by slow evaporation of the solutions at room temperature.

Compound (I)

Crystal data

$C_4H_{10}NO^+ \cdot C_7H_3ClNO_4^-$
 $M_r = 288.69$
Orthorhombic, $P2_12_12_1$
 $a = 10.304$ (2) Å
 $b = 19.557$ (6) Å
 $c = 6.4387$ (13) Å
 $V = 1297.5$ (5) Å³
 $Z = 4$
 $D_x = 1.478$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 11.3$ – 12.4°
 $\mu = 0.31$ mm⁻¹
 $T = 298$ K
Prismatic, colorless
0.40 × 0.30 × 0.20 mm

Data collection

Rigaku AFC-5R diffractometer
 ω - 2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.885$, $T_{\max} = 0.940$
4209 measured reflections
3101 independent reflections
1769 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.058$
 $\theta_{\text{max}} = 29.0^\circ$
 $h = -3 \rightarrow 14$
 $k = -3 \rightarrow 26$
 $l = -3 \rightarrow 8$
3 standard reflections
every 97 reflections
intensity decay: 1.7%

Refinement

Refinement on F^2
 $R(F) = 0.053$
 $wR(F^2) = 0.075$
 $S = 1.04$
3101 reflections
173 parameters
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + 0.4754P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.28$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0053 (9)
Absolute structure: (Flack, 1983),
1102 Friedel pairs
Flack parameter = 0.02 (8)

Table 1

Selected geometric parameters (Å, °) for (I).

Cl—C2	1.748 (3)	O3—N1	1.230 (3)
O1—C7	1.267 (3)	O4—N1	1.232 (3)
O2—C7	1.223 (4)		
O3—N1—C4—C3	−3.9 (4)	C2—C1—C7—O2	−74.1 (4)
O4—N1—C4—C3	176.2 (3)	C2—C1—C7—O1	108.9 (3)

Table 2

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

D—H...A	D—H	H...A	D...A	D—H...A
N2—H4...O1	0.89	1.80	2.682 (3)	170
N2—H5...O1 ⁱ	0.89	1.86	2.747 (3)	174
C6—H3...O3 ⁱⁱ	0.93	2.49	3.378 (4)	160
C10—H11...O5 ⁱⁱⁱ	0.97	2.55	3.486 (4)	161
C11—H12...O4 ^{iv}	0.97	2.53	3.340 (4)	141

Symmetry codes: (i) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$; (iii) $\frac{5}{2} - x, 1 - y, \frac{1}{2} + z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.

Compound (II)

Crystal data

C₄H₁₀NO⁺·C₇H₃ClNO₄[−]
M_r = 288.69
 Monoclinic, C2/c
a = 18.680 (6) Å
b = 10.498 (3) Å
c = 13.125 (3) Å
 β = 93.35 (2)°
V = 2569.5 (13) Å³
Z = 8

D_x = 1.492 Mg m^{−3}
 Mo K α radiation
 Cell parameters from 25 reflections
 θ = 11.2–12.5°
 μ = 0.32 mm^{−1}
T = 298 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} = 0.884, *T_{max}* = 0.940
 3215 measured reflections
 2945 independent reflections
 1741 reflections with *I* > 2 σ (*I*)

R_{int} = 0.025
 θ_{\max} = 27.5°
h = −1 → 24
k = 0 → 13
l = −17 → 17
 3 standard reflections
 every 97 reflections
 intensity decay: 1.5%

Refinement

Refinement on *F*²
R(*F*) = 0.046
wR(*F*²) = 0.121
S = 1.00
 2945 reflections
 225 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0219P)^2 + 1.0240P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.26 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e } \text{Å}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0240 (11)

Table 3

Selected geometric parameters (Å, °) for (II).

Cl—C2	1.743 (3)	O3—N1	1.216 (3)
O1—C7	1.247 (3)	O4—N1	1.218 (3)
O2—C7	1.244 (3)		
O3—N1—C5—C6	167.6 (2)	C2—C1—C7—O2	−63.1 (3)
O4—N1—C5—C6	−13.0 (4)	C2—C1—C7—O1	119.8 (3)

Table 4

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

D—H...A	D—H	H...A	D...A	D—H...A
N2—H4...O2	0.83 (3)	1.89 (3)	2.719 (3)	178 (2)
N2—H5...O1 ⁱ	1.00 (4)	1.77 (3)	2.753 (3)	169 (3)
C4—H2...O1 ⁱⁱ	0.89 (3)	2.58 (3)	3.371 (4)	148 (2)
C11—H13...O3 ⁱⁱⁱ	0.98 (3)	2.55 (3)	3.344 (4)	138 (2)

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

Compound (III)

Crystal data

C₄H₁₀NO⁺·C₇H₃ClNO₄[−]
M_r = 288.69
 Monoclinic, C2/c
a = 19.76 (2) Å
b = 10.085 (7) Å
c = 13.639 (5) Å
 β = 109.09 (4)°
V = 2569 (3) Å³
Z = 8

D_x = 1.493 Mg m^{−3}
 Mo K α radiation
 Cell parameters from 25 reflections
 θ = 11.1–12.4°
 μ = 0.32 mm^{−1}
T = 296 K
 Prismatic, colorless
 0.40 × 0.30 × 0.25 mm

Data collection

Rigaku AFC-5R diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
T_{min} = 0.884, *T_{max}* = 0.925
 3198 measured reflections
 2945 independent reflections
 1850 reflections with *I* > 2 σ (*I*)

R_{int} = 0.025
 θ_{\max} = 27.5°
h = −1 → 25
k = 0 → 13
l = −17 → 16
 3 standard reflections
 every 97 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R(*F*) = 0.047
wR(*F*²) = 0.116
S = 1.03
 2945 reflections
 225 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + 2.0068P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.25 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.20 \text{ e } \text{Å}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0053 (4)

Table 5

Selected geometric parameters (Å, °) for (III).

Cl—C4	1.727 (3)	O3—N1	1.220 (3)
O1—C7	1.242 (3)	O4—N1	1.204 (3)
O2—C7	1.237 (3)		
O4—N1—C3—C4	−20.3 (4)	C2—C1—C7—O2	−12.9 (4)
O3—N1—C3—C4	160.9 (3)	C2—C1—C7—O1	166.3 (2)

Table 6

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

D—H...A	D—H	H...A	D...A	D—H...A
N2—H4...O2	0.93 (3)	1.85 (3)	2.752 (4)	160 (3)
N2—H5...O1 ⁱ	0.99 (4)	1.66 (4)	2.629 (4)	164 (3)
C5—H2...O5 ⁱⁱ	1.00 (3)	2.58 (3)	3.269 (5)	125.9 (19)
C8—H6...O4 ⁱⁱⁱ	1.00 (4)	2.49 (4)	3.335 (6)	142 (3)
C10—H10...O2	1.05 (4)	2.48 (4)	3.255 (6)	131 (2)

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

For (I), the H atoms were treated as riding, with C–H = 0.93 Å for aromatic H, C–H = 0.97 Å for secondary H and N–H = 0.89 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{N})$. For (II) and (III), the H atoms were refined isotropically. Refined distances: C–H = 0.86 (3)–0.99 (3) Å and N–H = 0.83 (3)–0.99 (4) Å for (II); C–H = 0.89 (4)–1.05 (4) Å and N–H = 0.93 (3)–1.00 (3) Å for (III).

For all 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: *SHELXS97* (Sheldrick, 1990) for (I), and *SIR92* (Altomare *et al.*, 1993) for (II) and (III). For all compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *TEXSAN for Windows*.

X-ray measurements were carried out at the X-ray Laboratory of Okayama University.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1046). Services for accessing these data are described at the back of the journal.

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