Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3,5-Lutidinium–2-chloro-4-nitrobenzoate–2-chloro-4-nitrobenzoic acid (1/1/1)

Hiroyuki Ishida,* Bilkish Rahman and Setsuo Kashino

Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan

Correspondence e-mail: ishidah@cc.okayama-u.ac.jp

Received 20 August 2004
Accepted 26 August 2004
Online 4 September 2004

The title compound, $C_7H_{10}N^+\cdot C_7H_3ClNO_4^-\cdot C_7H_4ClNO_4$, consists of a 3,5-lutidinium (3,5-dimethylpyridinium) cation, a 2-chloro-4-nitrobenzoate anion and 2-chloro-4-nitrobenzoic acid. The anion is linked to the cation and the acid, respectively, by N—H···O and O—H···O hydrogen bonds. There are three C—H···O hydrogen bonds which connect the lutidinium–benzoate–benzoic acid units, forming a molecular tape.

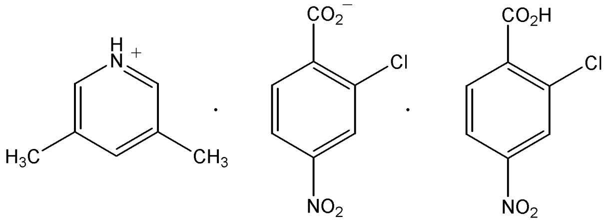
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.005 Å
R factor = 0.059
wR factor = 0.167
Data-to-parameter ratio = 16.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, (I), was investigated as part of a study on D—H···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*,*e*, 2002*a*,*b*,*c*). These systems are of interest in crystal engineering for the formation of chiral two-component molecular crystals (Koshima *et al.*, 1996; Ishida *et al.*, 2001*b*,*e*; Sugiyama *et al.*, 2002*a*,*b*). Furthermore, the systems are interesting candidates for a ^{35}Cl NQR relaxation study of proton transfer in hydrogen-bonded systems (Nihei *et al.*, 2000*a*,*b*). The present compound, (I), was accidentally obtained in the course of the preparation of the 3,5-lutidine–2-chloro-4-nitrobenzoic acid (1/1) complex, which was reported to represent the critical (inversion) point at 50% proton transfer in the O—H···N hydrogen bond (Habeeb & Awad, 1995; Awad & Habeeb, 1996).



(I)

In (I), the asymmetric unit is composed of three moieties, *viz*. $C_7H_{10}N^+$, $C_7H_3ClNO_4^-$ and $C_7H_4ClNO_4$ (Fig. 1). The benzoate anion is linked to the lutidinium cation and the benzoic acid, respectively, by N—H···O and O—H···O hydrogen bonds (Table 2). An acid–base interaction involving a proton transfer is observed between the cation and the anion; the critical point is not found in the present compound. The lutidinium–benzoate–benzoic acid units are linked by C—H···O hydrogen bonds (C15—H9···O6^{i}, C17—H10···O3^{ii} and C20—H13···O6^{i}; see Table 2 for details and symmetry codes) to form a molecular tape running in the $[11\bar{1}]$ direction (Fig. 2). A short contact [Cl2···O1^{i} = 3.120 (3) Å] is observed between the units. Neighboring tapes related by an inversion center are linked by a π–π stacking interaction between the

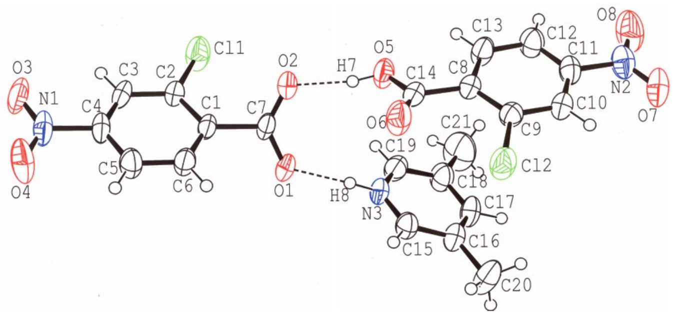


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of (I), with the atom-labeling. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level. N—H···O and O—H···O hydrogen bonds are indicated by dashed lines.

aromatic C1—C6 rings of benzoate ions (Fig. 3). The interplanar and centroid–centroid separations are 3.515 (2) and 3.658 (2) Å, respectively. The carboxylate group is twisted out of the plane of the benzene ring, probably due to the N—H···O and O—H···O hydrogen bonds; the dihedral angle between them is 49.45 (19)°. This may cause a close contact [O1···N1^{iv} = 2.853 (4) Å; symmetry code: (iv) $-x$, $-y$, $2 - z$] between the two tapes (Fig. 3). A similar non-hydrogen-bonding contact [O···N = 2.832 (3) Å] has been observed in benzimidazolium 2-chloro-4-nitrobenzoate (Ishida *et al.*, 2002*c*).

Experimental

Crystals of (I) were obtained by slow evaporation of an acetonitrile solution of 3,5-lutidine with 2-chloro-4-nitrobenzoic acid in a 1:1 molar ratio.

Crystal data

$C_7H_{10}N^+ \cdot C_7H_3ClNO_4^- \cdot C_7H_4ClNO_4$
$M_r = 510.28$
Triclinic, $P\overline{1}$
$a = 9.517$ (3) Å
$b = 9.9163$ (19) Å
$c = 13.194$ (5) Å
$\alpha = 75.30$ (2)°
$\beta = 70.12$ (3)°
$\gamma = 80.030$ (19)°
$V = 1127.5$ (6) Å^3
$Z = 2$
$D_x = 1.503$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.1$–12.3°
$\mu = 0.34$ mm^{-1}
$T = 296$ K
Prism, colorless
0.40 × 0.30 × 0.25 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.846$, $T_{max} = 0.918$
5486 measured reflections
5184 independent reflections
2574 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 27.5°$
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 0$
$l = -17 \rightarrow 16$
3 standard reflections every 97 reflections intensity decay: 2.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.167$
$S = 1.01$
5184 reflections
317 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.071P)^2 + 0.0055P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

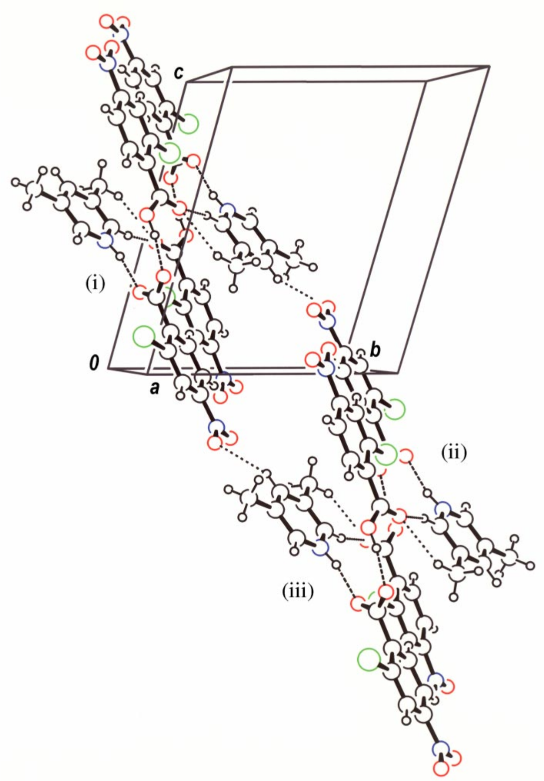


Figure 2
Packing diagram showing a molecular tape formed *via* N—H···O, O—H···O and C—H···O hydrogen bonds (shown as dashed lines). [Symmetry codes: (i) $1 - x$, $-y$, $1 - z$; (ii) $1 + x$, $1 + y$, $z - 1$; (iii) $2 - x$, $1 - y$, $-z$].

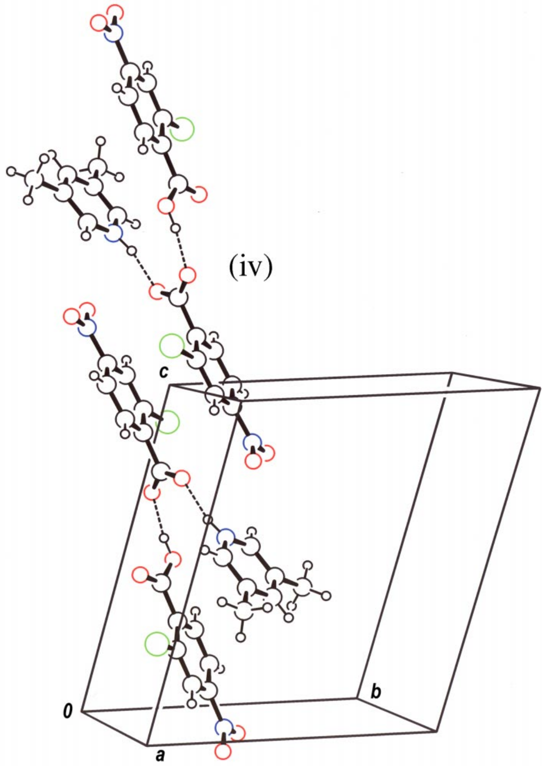


Figure 3
Packing diagram showing π–π stacking and a close N···O contact [symmetry code: (iv) $-x$, $-y$, $2 - z$].

o1662 Ishida *et al.* • $C_7H_{10}N^+ \cdot C_7H_3ClNO_4^- \cdot C_7H_4ClNO_4$ *Acta Cryst.* (2004). E**60**, o1661–o1663

Table 1
Selected geometric parameters (Å, °).

Cl1—C2	1.730 (3)	N2—C11	1.480 (4)
Cl2—C9	1.726 (3)	N3—C19	1.318 (4)
O1—C7	1.236 (4)	N3—C15	1.329 (4)
O2—C7	1.235 (4)	C1—C7	1.531 (4)
O5—C14	1.311 (4)	C8—C14	1.503 (4)
O6—C14	1.193 (4)	C16—C20	1.515 (5)
N1—C4	1.479 (4)	C18—C21	1.506 (5)
O1—C7—O2	128.4 (3)	C15—N3—C19	123.1 (3)
O5—C14—O6	124.1 (3)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H7···O2	0.87 (5)	1.70 (5)	2.542 (4)	163 (6)
N3—H8···O1	0.91 (4)	1.77 (4)	2.658 (4)	166 (4)
C15—H9···O6$^{\rm i}$	0.93	2.41	3.266 (5)	153
C17—H10···O3$^{\rm ii}$	0.93	2.48	3.350 (5)	156
C20—H13···O6$^{\rm i}$	0.96	2.51	3.390 (5)	153

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

H atoms attached to N and O atoms were refined isotropically. Other H atoms were treated as riding atoms, with C—H = 0.96 Å for the methyl groups and C—H = 0.93 Å for the benzene and pyridine rings. $U_{\rm iso}$(H) values were set at $1.5U_{\rm eq}$(C) for the methyl H atoms and at $1.2U_{\rm eq}$(C) for the other H atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1990); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (MSC, 1997–1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

X-ray measurements were made at the X-ray Laboratory of Okayama University. This work was supported by a Grant-in-Aid for Scientific Research (C) (No. 16550014) from the Ministry of Education, Science, Sports and Culture of Japan.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Awad, M. K. & Habeeb, M. M. (1996). *J. Mol. Struct.* **378**, 103–110.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Habeeb, M. M. & Awad, M. K. (1995). *Magn. Reson. Chem.* **33**, 476–480.

Ishida, H., Rahman, B. & Kashino, S. (2001*a*). *Acta Cryst.* C**57**, 876–879.

Ishida, H., Rahman, B. & Kashino, S. (2001*b*). *Acta Cryst.* C**57**, 1450–1453.

Ishida, H., Rahman, B. & Kashino, S. (2001*c*). *Acta Cryst.* E**57**, o627–o629.

Ishida, H., Rahman, B. & Kashino, S. (2001*d*). *Acta Cryst.* E**57**, o630–o632.

Ishida, H., Rahman, B. & Kashino, S. (2001*e*). *Acta Cryst.* E**57**, o744–o745.

Ishida, H., Fukunaga, T. & Kashino, S. (2002*a*). *Acta Cryst.* E**58**, o1081–o1082.

Ishida, H., Fukunaga, T. & Kashino, S. (2002*b*). *Acta Cryst.* E**58**, o1083–o1084.

Ishida, H., Fukunaga, T. & Kashino, S. (2002*c*). *Acta Cryst.* E**58**, o1085–o1087.

Koshima, H., Ding, K., Chisaka, Y. & Matsuura, T. (1996). *J. Am. Chem. Soc.* **118**, 12059–12065.

Molecular Structure Corporation (1990). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1997–1999). *TEXSAN for Windows*. Version 1.06. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.

Nihei, T., Ishimaru, S., Ishida, H., Ishihara, H. & Ikeda, R. (2000*a*). *Chem. Phys. Lett.* **329**, 7–14.

Nihei, T., Ishimaru, S., Ishida, H., Ishihara, H. & Ikeda, R. (2000*b*). *Chem. Lett.* pp. 1346–1347.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Sugiyama, T., Meng, J. & Matsuura, T. (2002*a*). *Enantiomer*, **7**, 397–404.

Sugiyama, T., Meng, J. & Matsuura, T. (2002*b*). *Mol. Cryst. Liq. Cryst.* **389**, 25–31.

Acta Cryst. (2004). E**60**, o1661–o1663 Ishida *et al.* • $C_7H_{10}N^+\cdot C_7H_3ClNO_4^-\cdot C_7H_4ClNO_4$ **o1663**