Acta Crystallographica Section E
**Structure Reports**
**Online**

ISSN 1600-5368

# Piperidinium *p*-nitrobenzoate

**Yoshimitsu Moritani,[a]† Akihiko Takeda[b] and Setsuo Kashino[b]***

[a]Graduate School of Natural Science and Technology, Okayama University, Tsushima, Okayama 700-8530, Japan, and [b]Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700-8530, Japan

† On leave from Mitsui Chemical Analysis and Consulting Service Inc., Waki 6-1-2, Waki-cho, Kuga-gun, Yamaguchi 740-0061, Japan.

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

**Key indicators**

Single-crystal X-ray study
*T* = 298 K
Mean σ(C–C) = 0.005 Å
*R* factor = 0.057
*wR* factor = 0.205
Data-to-parameter ratio = 14.6

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

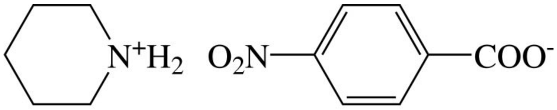
Received 22 June 2001
Accepted 28 June 2001
Online 13 July 2001

A new type of hydrogen-bond pattern for piperidinium *p*-substituted benzoates is reported; this is found in piperidinium *p*-nitrobenzoate, $C_5H_{12}N^+\cdot C_7H_4NO_4^-$, (I). In the crystal of (I), the cations and anions are linked by N—H···O hydrogen bonds around a center of symmetry to form a cyclic dimer of the formula unit.

## Comment

We report here a new type of hydrogen-bond pattern in the cyclic secondary amine–*p*-substituted benzoic acid (1/1) system. In piperidinium *p*-nitrobenzoate, (I), a centrosymmetric dimer of the formula unit is formed through N—H···O hydrogen bonds (Fig. 1 and Table 1).

In most crystalline salts formed between cyclic secondary amines and *p*-substituted benzoic acids, the cations and anions are arranged around a twofold screw axis to form N—H···O hydrogen bonds (Kashino *et al.*, 1972, 1978, 1981; Kashino, 1973). The same type of hydrogen bonding is also found in both pyrrolidinium *p*-nitrobenzoate and hexamethyleneiminium *p*-nitrobenzoate (Takeda, 1992). In a few cases, the cations and anions are arranged along a glide plane to form N—H···O hydrogen bonds (Kashino *et al.*, 1973, 1981).



(I)

The possibility of the formation of a cyclic dimer through the N—H···O hydrogen bonds was deduced based on the result of a molecular weight measurement in benzene solution, combined with a geometrical consideration of the hydrogen-bonded system (Kashino, 1973). However, the formation of a cyclic dimer has been found only in one of the dimorphs of hexamethyleneiminium *p*-bromobenzoate, in which the dimer is formed around a twofold axis (Kashino *et al.*, 1981). The present study established a centrosymmetric type as the fourth pattern of hydrogen bonding possible in salts of cyclic secondary amines and *p*-substituted benzoic acids.

## Experimental

Stoichiometric amounts of piperidine and *p*-nitrobenzoic acid were dissolved in benzene at 340 K. After cooling the solution, crystals of (I) were grown by slow evaporation at room temperature.

*Crystal data*

$C_5H_{12}N^+\cdot C_7H_4NO_4^-$
$M_r = 252.27$
Orthorhombic, *Pccn*
$a = 8.949$ (2) Å
$b = 22.451$ (5) Å
$c = 12.712$ (4) Å
$V = 2554.0$ (11) Å$^3$
$Z = 8$
$D_x = 1.312$ Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 10.6$–11.4°
$\mu = 0.10$ mm$^{-1}$
$T = 298$ K
Prismatic, colorless
0.50 × 0.30 × 0.20 mm

*Data collection*

Rigaku AFC-5*R* diffractometer
*ω*–2*θ* scans
Absorption correction: *ψ* scan (North *et al.*, 1968)
$T_{\rm min} = 0.952$, $T_{\rm max} = 0.980$
2875 measured reflections
2509 independent reflections
1142 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\rm max} = 26.0°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 27$
$l = 0 \rightarrow 15$
3 standard reflections every 97 reflections
intensity decay: 0.6%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.205$
$S = 0.91$
2509 reflections
172 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 1.1042P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.13$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.18$ e Å$^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0059 (14)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| O1—C7 | 1.253 (4) | C3—C4 | 1.377 (5) |
| O2—C7 | 1.250 (4) | C4—C5 | 1.379 (5) |
| O3—N1 | 1.219 (4) | C5—C6 | 1.378 (5) |
| O4—N1 | 1.216 (4) | N2—C8 | 1.478 (5) |
| N1—C4 | 1.476 (5) | N2—C12 | 1.489 (5) |
| C1—C6 | 1.386 (5) | C8—C9 | 1.510 (6) |
| C1—C2 | 1.387 (5) | C10—C11 | 1.502 (6) |
| C1—C7 | 1.513 (5) | C11—C12 | 1.500 (6) |
| C2—C3 | 1.378 (5) | | |
| O4—N1—O3 | 123.6 (4) | C6—C5—C4 | 118.5 (3) |
| O4—N1—C4 | 118.5 (4) | C5—C6—C1 | 120.9 (3) |
| O3—N1—C4 | 117.9 (4) | O2—C7—O1 | 125.0 (4) |
| C6—C1—C2 | 119.4 (3) | O2—C7—C1 | 117.7 (3) |
| C6—C1—C7 | 120.5 (3) | O1—C7—C1 | 117.2 (3) |
| C2—C1—C7 | 120.1 (3) | C8—N2—C12 | 111.1 (3) |
| C3—C2—C1 | 120.3 (3) | N2—C8—C9 | 109.6 (4) |
| C4—C3—C2 | 119.1 (3) | C10—C9—C8 | 110.0 (4) |
| C3—C4—C5 | 121.8 (4) | C11—C10—C9 | 111.0 (3) |
| C3—C4—N1 | 119.2 (3) | C12—C11—C10 | 111.4 (4) |
| C5—C4—N1 | 119.0 (4) | N2—C12—C11 | 110.3 (3) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H5···O1 | 0.94 (4) | 1.78 (4) | 2.697 (5) | 165 (4) |
| N2—H6···O2$^{\rm i}$ | 1.02 (5) | 1.71 (5) | 2.731 (4) | 171 (4) |

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

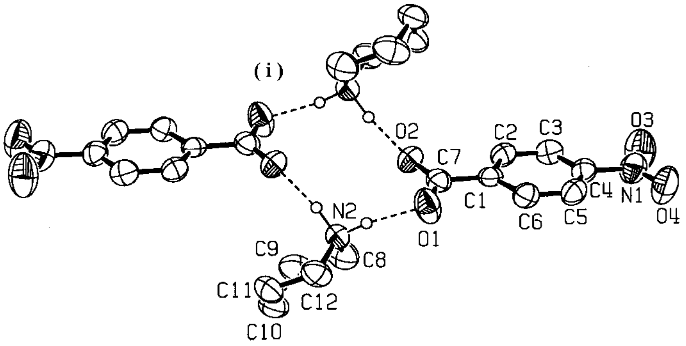


**Figure 1**
A molecular view of (I) showing the hydrogen-bonding pattern and the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms involved in hydrogen bonds are shown as small spheres of arbitrary radii. Hydrogen bonds are indicated by dashed lines. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

All H atoms were found from a difference Fourier map. At the final stage of the least-squares refinement, all H atoms except those involved in hydrogen bonds were fixed at the ideal positions, and their isotropic displacement parameters were fixed to $1.2U_{\rm eq}$ of the parent atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *TEXSAN* for Windows.

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