Experimental

A commercial sample of the title compound (Sigma Chemicals) was recrystallized from aqueous solution by slow evaporation of the solvent at room temperature.

Crystal data

$C_6H_8N_2O_3 \cdot H_2O$	Mo $K\alpha$ radiation
$M_r = 174.156$	$\lambda = 0.71069$ Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
$a = 7.756\,(6)$ Å	$\theta = 18.25-22.15°$
$b = 17.107\,(2)$ Å	$\mu = 0.113$ mm^{-1}
$c = 6.090\,(2)$ Å	$T = 296$ K
$V = 808.1\,(6)$ Å^3	Plate
$Z = 4$	$0.4 \times 0.3 \times 0.1$ mm
$D_x = 1.431$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Rigaku AFC-5R diffractometer	1100 reflections with $I > 0$
$\omega/2\theta$ scans	$\theta_{max} = 27.5°$
Absorption correction:	$h = 0 \rightarrow 9$
ψ-scan (North et al., 1968)	$k = 0 \rightarrow 22$
	$l = 0 \rightarrow 7$
$T_{min} = 0.97$, $T_{max} = 1.00$	3 standard reflections
1120 measured reflections	every 150 reflections
1120 independent reflections	intensity decay: 0.73%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R(F) = 0.060$	$\Delta\rho_{max} = 0.38$ e Å^{-3}
$wR(F^2) = 0.107$	$\Delta\rho_{min} = -0.20$ e Å^{-3}
$S = 1.44$	Extinction correction: none
1100 reflections	Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
117 parameters	
H atoms: see below	
$w = 4F_o^2/\sigma^2(F_o^2)$	

Table 1. *Selected bond lengths (Å)*

O1—C8	1.244 (3)	N3—C4	1.366 (4)
O2—C8	1.246 (3)	C4—C5	1.357 (4)
O3—C7	1.410 (3)	C4—C6	1.488 (4)
N1—C2	1.314 (4)	C6—C7	1.533 (4)
N1—C5	1.364 (4)	C7—C8	1.541 (4)
N3—C2	1.330 (3)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1^i	0.947	1.818	2.677 (3)	149.4 (2)
N3—H3$\cdots$O2^{ii}	0.949	1.780	2.716 (3)	169.0 (2)
O3—H8$\cdots$O4	0.925	1.812	2.734 (4)	174.6 (1)
O4—H9$\cdots$O1^{iii}	0.98 (3)	1.79 (3)	2.751 (3)	166 (3)
O4—H10$\cdots$O2^{iv}	0.79 (4)	1.97 (4)	2.760 (3)	176 (4)

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

H atoms were fixed, except for those on H_2O, which were freely refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Pro-

gram(s) used to solve structure: *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*.

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A 1:1 complex of 4-nitropyridine *N*-oxide and 3-hydroxybenzoic acid

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Abstract

The title molecular complex, $C_5H_4N_2O_3 \cdot C_7H_6O_3$, is hydrogen bonded, the molecules being linked by an O—H$\cdots$O hydrogen bond between the phenol hydroxyl group and the *N*-oxide O atom [O$\cdots$O 2.642 (2) Å].

The 3-hydroxybenzoic acid molecules form hydrogen-bonded pairs across centres of symmetry in the complex, with an O···O distance of 2.628 (2) Å. The interplanar angle between the aromatic rings in the two components is 63.86 (6)°.

Comment

This work is part of an ongoing study of several series of molecular complexes obtained from 4-nitropyridine *N*-oxide (NPNO) with diverse hydrogen-bond donors (Moreno-Fuquen *et al.*, 1996). Given that 3-hydroxybenzoic acid (MHBA) is a good hydrogen-bond donor, the formation of the title complex with the NPNO molecule was undertaken. The crystal structure of MHBA has been reported by Gridunova *et al.* (1982). The relatively high melting point [475 (1) K] of the title complex strongly suggests the existence of dimers in the crystal. Formation of cyclic hydrogen bond dimers is the most common behaviour of carboxylic acid molecules (Leiserowitz, 1976). The crystal and molecular structure of the NPNO·MHBA system has been determined in order to establish if this type of hydrogen bond is formed in this particular complex, to study whether the hydrogen-bonded cycle of the dimer is broken by the formation of the complex, and to explore the possible non-linear optical properties of the complex.
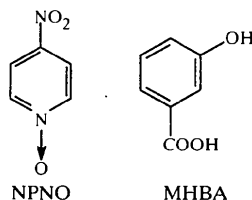
$$\text{NPNO} \qquad \text{MHBA}$$

Fig. 1 shows the hydrogen-bonded complex of NPNO·MHBA, with the adopted atom-numbering scheme. The complex owes its formation to a moderate intermolecular hydrogen bond (Emsley, 1984) between O1 of the *N*-oxide group of NPNO and O4 of the hydroxyl group of MHBA, with an O1···O4 distance of 2.642 (2) Å and an O1···HO4—O4 angle of 169 (3)°. The O4—H4 and O1···HO4 distances are 0.95 (3) and 1.71 (3) Å, respectively. The interplanar angle between the aromatic rings in NPNO and MHBA in this complex is 63.86 (6)°. The screw-related NPNO is almost parallel to MHBA, with a dihedral angle of 4 (2)°. Bond lengths and angles (Table 1) found in this study are similar to those reported for the free NPNO molecule (Eichhorn, 1956; Wang *et al.*, 1976). The parameters of MHBA in the title complex may be compared with those of the free structural modification I of 3-hydroxybenzoic acid, a monoclinic structure which exists as a dimer (Gridunova *et al.*, 1982). The C11—O4 distance of the hydroxyl group changes from 1.359 (2) Å in the title complex to

1.388 (2) Å in the free molecule. The C6—O6 and C6—O5 distances of 1.291 (2) and 1.246 (3) Å, respectively, in the title complex may be compared with the values of 1.260 (2) and 1.269 (3) Å, respectively, in structural modification I. The C—O bond lengths of the carboxyl group in structural modification I are therefore very close; the greater difference in C—O bond lengths of the carboxyl group in the title complex is as expected for an ordered COOH group. The cyclic hydrogen-bonded dimer is found even after the formation of the complex, showing the following interactions: O6···O5^i 2.628 (2), O6—HO6 1.01 (3) and HO6···O5^i 1.62 (3) Å, and O6—HO6···O5^i 176 (2)° [symmetry code: (i) $1 - x$, $-y$, $1 - z$]. This result coincides with the behaviour of benzoic acid derivatives, typically self-assembled as centrosymmetric dimers (Frankenbach & Etter, 1992). The present complex forms an alternate stacking of NPNO and MHBA, resulting in a herring-bone packing structure approximately in the [010] direction, with mean interplanar distances between the overlapped rings of 3.311 (2) Å [for the molecule at $(-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$] and 3.111 (2) Å [for the molecule at $(-\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$].
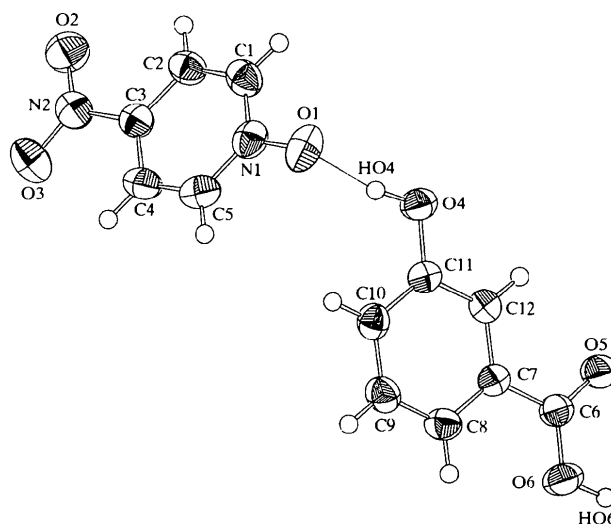

Fig. 1. A *ZORTEP* plot (Zsolnai, 1995) of the title complex, with the atomic labelling scheme. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

The synthesis of the title complex was carried out by slow evaporation from an equimolar solution of NPNO and MHBA in acetonitrile.

Crystal data

$C_5H_4N_2O_3\cdot C_7H_6O_3$ Mo $K\alpha$ radiation
$M_r = 278.22$ $\lambda = 0.71073$ Å

Monoclinic
$P2_1/n$
$a = 6.5453\,(6)$ Å
$b = 7.5995\,(8)$ Å
$c = 24.855\,(3)$ Å
$\beta = 95.46\,(2)°$
$V = 1230.7\,(2)$ Å^3
$Z = 4$
$D_x = 1.502$ Mg m^{-3}
D_m not measured

Cell parameters from 25
  reflections
$\theta = 9.9–18.2°$
$\mu = 0.12$ mm^{-1}
$T = 293$ K
Prism
$0.15 \times 0.12 \times 0.10$ mm
Pale yellow

Data collection

Enraf–Nonius CAD-4
  diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2719 measured reflections
2495 independent reflections
1613 reflections with
  $I > 2\sigma(I)$

$R_{int} = 0.019$
$\theta_{max} = 26.29°$
$h = 0 \rightarrow 8$
$k = -9 \rightarrow 0$
$l = -30 \rightarrow 30$
3 standard reflections
  frequency: 120 min
  intensity decay: 0.70%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.117$
$S = 1.114$
2493 reflections
188 parameters
H atoms: see below
$w = 1/(\sigma^2(F_o^2) + (0.0306P)^2 + 0.6014P)$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.221$ e Å^{-3}
$\Delta\rho_{min} = -0.167$ e Å^{-3}
Extinction correction:
  SHELXL93 (Sheldrick,
  1993)
Extinction coefficient:
  0.054 (3)
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

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

O1—N1	1.310 (2)	O6—C6	1.291 (2)
N1—C5	1.353 (3)	O6—HO6	1.01 (3)
N1—C1	1.354 (3)	C6—C7	1.478 (3)
N2—C3	1.467 (3)	C7—C12	1.389 (3)
O4—C11	1.359 (2)	C7—C8	1.390 (3)
O4—HO4	0.95 (3)	C10—C11	1.391 (3)
O5—C6	1.246 (3)	C11—C12	1.383 (3)
O1—N1—C5	119.8 (2)	C12—C7—C8	120.3 (2)
O1—N1—C1	119.8 (2)	C12—C7—C6	119.0 (2)
C5—N1—C1	120.4 (2)	C8—C7—C6	120.7 (2)
C6—O6—HO6	113.7 (15)	O4—C11—C12	117.6 (2)
O5—C6—O6	122.6 (2)	O4—C11—C10	122.4 (2)
O5—C6—C7	120.9 (2)	C12—C11—C10	119.9 (2)
O6—C6—C7	116.5 (2)		

The ring H atoms were added at calculated positions and refined using a riding model with *SHELXL93* (Sheldrick, 1993) defaults (C—H 0.93 Å). A B_{iso} value of 6.0 Å^2 was assigned to all H atoms. Atom HO4 was located from a difference Fourier map and its coordinates were refined.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (Frenz, 1978). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SDP*.

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1-(*tert*-Butyl)-3-(2-pyridyl)thiourea

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Abstract

In the title compound, $(CH_3)_3CNHCSNH(C_5H_4N)$ (or $C_{10}H_{15}N_3S$), the *endo*-N···imino-N distance of 2.668 (2) Å is indicative of intramolecular hydrogen bonding. The pyridyl ring and the thiourea plane are inclined at an angle of 13.29 (9)°. The molecules are dimerized through a pair of hydrogen bonds of the type C=S···H—N.