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2:1 Complex of 3-Picoline *N*-Oxide and Hydroquinone

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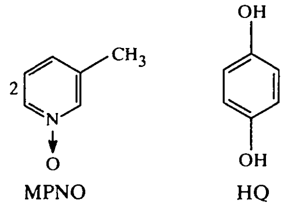
Abstract

The title system, $2C_6H_7NO.C_6H_6O_2$, belongs to a series of molecular complexes formed from 3-picoline *N*-oxide and diverse hydrogen-bond donors. The molecular complex owes its formation to a hydrogen bond between the O atom of the *N*-oxide group of each 3-picoline *N*-oxide molecule and the O atom of an OH group of the hydroquinone molecule. The complex has a dihedral angle of 48.16 (5)° between the aromatic rings and exhibits overlap between the hydroquinone and 3-picoline *N*-oxide molecules in the [001] direction. The structural characteristics of the title complex are compared with those of similar systems.

Comment

The present work complements a series of studies of non-centrosymmetric molecular complexes of 3-picoline *N*-oxide (MPNO) with diverse hydrogen-bond donors (HBD), which can be used as non-linear optical materials (Prasad & Williams, 1991). Though the present molecular system is centrosymmetric, information about its crystal structure is very important to the study of the general behaviour of MPNO with respect to its formation of hydrogen-bonded complexes. MPNO and molecular complexes such as MPNO–*p*-toluic acid (MPNO–PTOL) (Moreno-Fuquen *et al.*, 1997) may be taken as a reference frame for analysing the behaviour of the present complex. The isomeric molecular complexes formed by 2-picoline *N*-oxide and hydroquinone (HQ) (OPNO–HQ), and by 4-picoline *N*-oxide and HQ (PPNO–HQ) are isostructural, with space group *Cc*, and display identical and atypical crystal packing (Moreno-Fuquen *et al.*, 1998). Indeed, the O atom of the *N*-oxide group is simultaneously linked to two hydroxides of two neighbouring HQ molecules, forming infinite chains in the [101] direction. This behaviour is not observed in the isomeric title complex, in which the HQ molecule is linked to two MPNO molecules *via* its OH groups.



A displacement ellipsoid plot of the hydrogen-bonded complex with the atom-numbering scheme is shown in Fig. 1. The complex is linked by a hydrogen bond between the O1 atom of the *N*-oxide group of each MPNO molecule and the O2 atom of a hydroxide group of the HQ molecule, with an O···O distance of 2.621 (2) Å and an O2—HO2···O1 angle of 173 (2)°. This system may be described by two planes formed by the aromatic rings, which have a dihedral angle of 48.16 (5)° between them. The bond lengths and angles of the MPNO molecule are similar to those observed in the MPNO–PTOL system (Moreno-Fuquen *et al.*, 1997). The bond lengths and angles of the HQ molecule in the complex are similar to those reported for the free molecule (Maartmann-Moe, 1966).

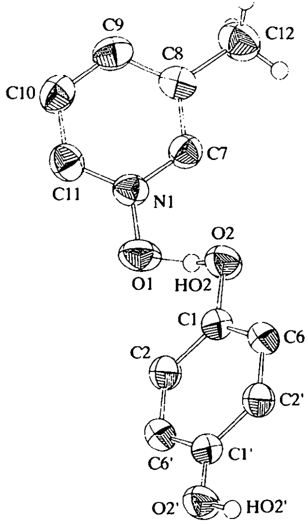


Fig. 1. A perspective view of the title complex with the atomic labelling scheme. Displacement ellipsoids are plotted at the 50% probability level. The ring H atoms have been omitted for clarity.

A view of the crystal packing is presented in Fig. 2. The MPNO and HQ rings are overlapped in the [001] direction with mean distances between the rings of 3.555 (9) (symmetry code: $\frac{3}{2}-x, \frac{3}{2}+y, \frac{3}{2}-z$) and 3.696 (9) Å (symmetry code: $-\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z$).

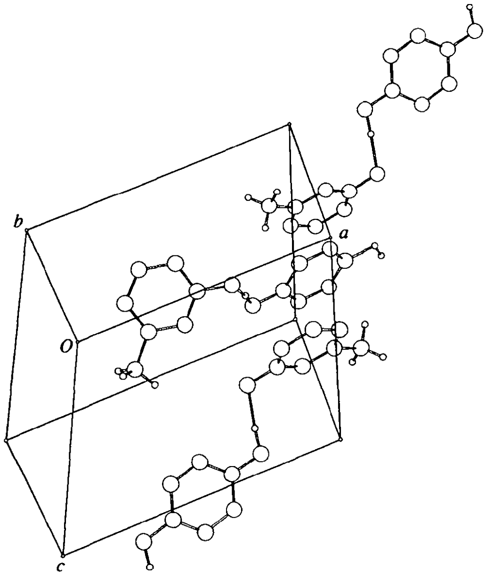


Fig. 2. View of the packing showing the overlapped rings along the [001] direction.

Experimental

The synthesis of the title complex was carried out by slow evaporation of an equimolecular solution of MPNO and HQ in acetonitrile.

Crystal data

$2C_6H_7NO.C_6H_6O_2$
$M_r = 328.37$
Monoclinic
$P2_1/n$
$a = 11.2065\,(5)$ Å
$b = 6.0273\,(4)$ Å
$c = 12.7077\,(5)$ Å
$\beta = 105.10\,(3)°$
$V = 828.69\,(7)$ Å^3
$Z = 2$
$D_x = 1.316$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.34–18.23°$
$\mu = 0.09$ mm^{-1}
$T = 295$ K
Transparent prism
0.22 × 0.18 × 0.12 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1759 measured reflections
1683 independent reflections
1446 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.012$
$\theta_{\rm max} = 26.29°$
$h = -13 \rightarrow 13$
$k = -7 \rightarrow 0$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: 0.71%

Refinement

Refinement on F^2
$R(F) = 0.040$
$wR(F^2) = 0.123$
$S = 0.988$
1683 reflections
113 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0849P)^2 + 0.1853P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.205$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.184$ e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.032 (7)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

O1—N1	1.3262 (15)	O2—C1	1.364 (2)
N1—C11	1.343 (2)	C1—C2	1.387 (2)
N1—C7	1.351 (2)	C1—C6	1.388 (2)
C8—C12	1.508 (2)		
O1—N1—C11	119.32 (13)	N1—C11—C10	119.59 (14)
O1—N1—C7	119.56 (13)	O2—C1—C2	122.82 (13)
C11—N1—C7	121.12 (13)	O2—C1—C6	118.52 (13)
C7—C8—C12	119.7 (2)	C2—C1—C6	118.66 (13)
C9—C8—C12	121.88 (14)		

The ring and methyl H atoms were included at geometrically idealized positions. The HO2 atom was located from a difference Fourier map and its coordinates were refined. An isotropic displacement parameter of 6.0 Å^2 was assigned to each H atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP-VAX* (Frenz, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SDP-VAX*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1345). Services for accessing these data are described at the back of the journal.

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1:1 Complex of 2-Aminobenzoic Acid and 3-Methyl-4-nitropyridine *N*-Oxide

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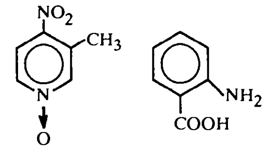
Abstract

The structure analysis of the title molecular complex, $C_7H_7NO_2.C_6H_6N_2O_3$, forms part of an ongoing study of the design of non-centrosymmetric systems based on 3-methyl-4-nitropyridine *N*-oxide. The title complex is held together by a hydrogen bond between the O atom of the *N*-oxide group and the O atom of the OH group of the 2-aminobenzoic acid molecule. In the crystal, the complexes overlap in the [100] direction.

Comment

A series of molecular complexes of 4-nitropyridine *N*-oxide and picoline *N*-oxide derivatives with diverse hydrogen-bond donors have been studied in recent years in order to obtain new materials with possible non-linear optical (NLO) properties (Moreno-Fuquen, De Almeida Santos & Lechat, 1996; Moreno-Fuquen, De Almeida Santos & Gambardella, 1996). Within the family of crystals having the *N*-oxide group, the 3-methyl-4-nitropyridine *N*-oxide (POM) molecular system is one of the best electro-optic materials in the visible range (Sapriel *et al.*, 1989). NLO properties of metal–halide complexes with the organic ligand POM have been reported (Hu *et al.*, 1992, 1994). In the present work, a molecular complex obtained from POM and one hydrogen-bond donor, namely 2-aminobenzoic acid (OABA), is described for the first time.



POM OABA

A *ZORTEP* (Zsolnai, 1995) diagram of the hydrogen-bonded complex is shown in Fig. 1. The complex is held together by a hydrogen bond between the O1 atom of the *N*-oxide group of the POM molecule and the O4 atom of the carboxylic group of the OABA molecule, with an O···O distance of 2.601 (3) Å and an O4—HO4···O1 angle of 160 (3)°.

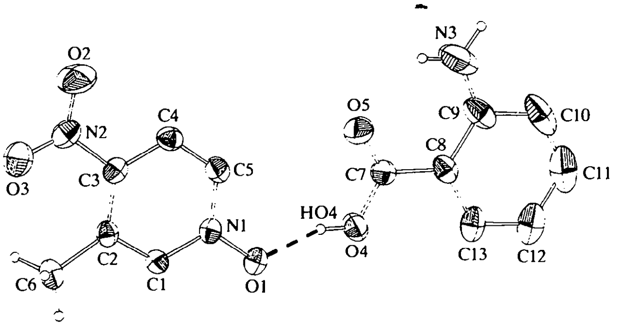


Fig. 1. A perspective view of the title complex with the atomic labelling scheme. Displacement ellipsoids are plotted at the 30% probability level. The ring H atoms have been omitted for clarity.

In the title structure, the O5 atom is intramolecularly hydrogen bonded to the amine HN31 atom, with an O5···N3 distance of 2.728 (4) Å. This distance is greater than the corresponding distances in free OABA molecules [2.688 (4) Å in the monoclinic form and 2.682 (7) Å in the orthorhombic form]. There is also an intermolecular hydrogen bond between the N3 atom (at x, y, z) and an O5 atom (symmetry code: $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$), with an N3···O5 distance of 3.121 (4) Å. The other bond lengths and angles observed in this complex are similar to those reported for free OABA molecules (Takazawa *et al.*, 1986; Boone *et al.*, 1977).

The internal parameters of POM in the complex are similar to those of the free molecule (Shiro *et al.*, 1977). They are also similar to those reported for metal–halide complexes in which POM is an organic ligand (Hu *et al.*, 1994).

A *ZORTEP* view (Zsolnai, 1995) of the crystal packing is presented in Fig. 2. The POM and OABA rings show an *ABAB* disposition and are overlapped with mean distances between the rings of 3.483 (3) (symmetry code: $x-1, y+1, z$) and 3.374 (3) Å (symmetry code: $x, y+1, z$) along the [100] direction. There are no nitro–amino interactions in this complex. This is contrary to what is observed in nitroanilines and their analogues (Panunto *et al.*, 1987).