Absorption correction: none
9439 measured reflections
4535 independent reflections
2319 reflections with $I > 2\sigma(I)$

$h = -10 \rightarrow 7$
$k = -21 \rightarrow 16$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R(F) = 0.034$
$wR(F^2) = 0.050$
$S = 0.950$
4535 reflections
366 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0141P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.139$ e Å^{-3}
$\Delta\rho_{\min} = -0.111$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Data were collected applying an imaging-plate system with the following measurement parameters yielding data completenesses of typically 0.9: detector distance 75–80 mm; irradiation/exposure 12–25 min; $0 < \varphi < 94°$. Methyl H atoms were placed in idealized positions based on difference electron synthesis and torsion angles were refined with fixed isotropic displacement parameters of $1.5U_{\rm eq}$(parent C). All other H atoms were placed in idealized positions and refined with fixed isotropic displacement parameters of $1.2U_{\rm eq}$(parent C). Atom C44 of compound (VII) is disordered and was refined using a split model.

For all compounds, program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *PLATON*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1241). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Breu, J., Range, K. J., Riebel, P., Weber, A. & Sauer, J. (1996). *Acta Cryst.* C**52**, 2053–2056.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Hesse, M., Meier, H. & Zeeh, B. (1995). In *Spektroskopische Methoden in der Organischen Chemie*. Stuttgart: Georg Thieme Verlag.

Huisgen, R. (1984). *1,3-Dipolar Cycloadditions – Introduction, Survey, Mechanism*, edited by A. Padwa, pp. 63–76. New York: John Wiley.

Huisgen, R. (1988). *Steric Course and Mechanism of 1,3-Dipolar Cycloadditions. Advances in Cycloadditions*, Vol. 1, pp. 1–31. New York: JAI Press.

Riebel, P., Weber, A., Troll, T., Sauer, J. & Breu, J. (1996). *Tetrahedron Lett.* pp. 1583–1586.

Riebel, P., Weber, A., Troll, T., Sauer, J., Breu, J. & Nöth, H. (1996). *Tetrahedron Lett.* pp. 1587–1590.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Weber, A. (1997). PhD thesis, University of Regensburg, Germany.

Weber, A. & Sauer, J. (1998). *Tetrahedron Lett.* In the press.

Woodward, R. B. & Hoffmann, R. (1969). *Angew. Chem. Int. Ed. Engl.* **8**, 781–853.

Acta Cryst. (1998). C**54**, 513–515

Pyridine *N*-Oxide and 4-Nitrophenol (1:1 Complex)

Rodolfo Moreno-Fuquen,[a] Regina Helena De Almeida Santos[b] and Regina Helena Porto Francisco[b]

[a]*Departamento de Química, Facultad de Ciencias, Universidad del Valle, Apartado 25360, Cali, Valle, Colombia, and* [b]*DQFM Instituto de Química de São Carlos, Universidade de São, Paulo, CEP 13560.250, São Carlos, SP, Brazil. E-mail: fuquen@iqsc.sc.usp.br*

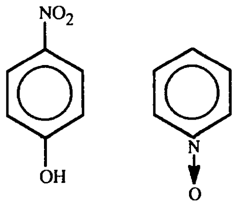
(*Received 16 July 1997; accepted 13 October 1997*)

Abstract

In the title hydrogen-bonded complex, $C_5H_5NO.C_6H_5NO_3$, the two components are linked by an O—H···O hydrogen bond between the phenol hydroxyl group and the *N*-oxide O atom [O···O 2.553 (2) Å]. The interplanar angle between the aromatic rings in the two components is 41.29 (6)°.

Comment

The present work is part of a structural study of molecular complexes of *N*-oxide systems with hydrogen-bond donors and we report here on the structure of the 1:1 complex between pyridine *N*-oxide (PNO) and 4-nitrophenol (PNP). A similar series of molecular complexes formed from 4-nitropyridine *N*-oxide and diverse hydrogen-bond donors, which observes the possibility of application in non-linear optics, has been reported previously (Moreno-Fuquen *et al.*, 1996, and references therein).



PNP PNO

The crystallographic data of the free PNO molecule (Ülkü *et al.*, 1971) can be used as a comparison for the parameters obtained for the title complex. A *ZORTEP* (Zsolnai, 1995) view of the hydrogen-bonded PNO.PNP complex and its numbering scheme are shown in Fig. 1. The molecular complex owes its formation to a hydrogen bond between the O4 atom of the *N*-oxide group of PNO and the O1 atom of the O—H group of PNP; the dimensions are O1···O4 2.553 (2), O1—

Acta Crystallographica Section C
ISSN 0108-2701 © 1998

H1 0.95 (2) HO1···O4 1.61 (2) Å and O1—HO1···O4 174 (2)°. From the O···O value, the strength of the hydrogen bond is classified as strong (Emsley, 1984). The interplanar angle between the aromatic rings in PNO and PNP in the present complex is 41.29 (6)°. Bond lengths and angles (Table 1) are similar to those reported for the free PNO molecule (Ülkü *et al.*, 1971) and the free PNP molecule (Coppens & Schmidt, 1965*a*,*b*).

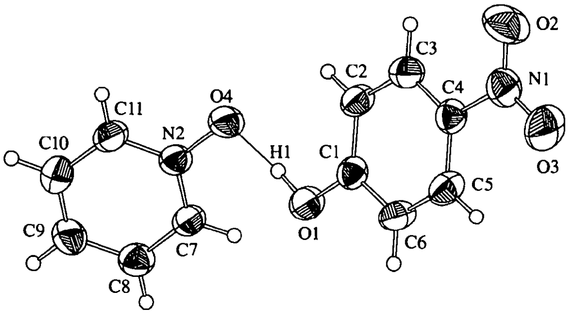


Fig. 1. Representation of the hydrogen-bonded title complex showing the atomic numbering. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Crystals of the title complex were prepared by slow evaporation from an equimolecular solution of PNO and PNP in acetonitrile. Regular pale-yellow crystals were obtained with an m.p. of 387 (2) K.

Crystal data

$C_5H_5NO.C_6H_5NO_3$
$M_r = 234.21$
Monoclinic
$P2_1/c$
$a = 7.983$ (4) Å
$b = 6.054$ (3) Å
$c = 22.595$ (1) Å
$\beta = 95.74$ (1)°
$V = 1086.5$ (8) Å^3
$Z = 4$
$D_x = 1.432$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.6$–18.2°
$\mu = 0.111$ mm^{-1}
$T = 253$ K
Transparent prism
0.23 × 0.12 × 0.05 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4400 measured reflections
2203 independent reflections
1521 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.036$
$\theta_{\rm max} = 26.31$°
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 7$
$l = -28 \rightarrow 28$
3 standard reflections
frequency: 120 min
intensity decay: 0.53%

Refinement

Refinement on F^2
$R(F) = 0.038$
$wR(F^2) = 0.100$
$S = 0.947$
2202 reflections
158 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 0.3324P]$, $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.193$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.242$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.012 (2)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

O1—C1	1.336 (2)	N1—C4	1.446 (2)
O1—H1	0.95 (3)	O4—N2	1.325 (2)
O2—N1	1.226 (2)	N2—C11	1.346 (2)
O3—N1	1.232 (2)	N2—C7	1.348 (2)
O2—N1—O3	122.5 (2)	C5—C4—N1	118.9 (2)
O2—N1—C4	119.2 (2)	C3—C4—N1	119.8 (2)
O3—N1—C4	118.3 (2)	O4—N2—C11	119.10 (14)
O1—C1—C6	117.7 (2)	O4—N2—C7	120.09 (15)
O1—C1—C2	122.8 (2)		

The ring H atoms were added at calculated positions and were refined using a riding model with *SHELXL*93 (Sheldrick, 1993) defaults (C—H 0.93–0.96 Å); they were given isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameters of their attached atom. The hydroxyl H atom, H1, was located from a Fourier difference map and its coordinates were refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *VAXSDP* (Frenz, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *VAXSDP*.

The authors thank Professor E. Castellano of the IFSC/USP for the fruitful discussions about this work. One of the authors (RMF) wishes to acknowledge financial support from the Brazilian agency FAPESP, Grant 1996/7490-6. The authors also thank FINEP (Brazil) and Universidad del Valle (Colombia) and COLCIENCIAS for partial financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1373). Services for accessing these data are described at the back of the journal.

References

Coppens, P. & Schmidt, G. M. J. (1965*a*). *Acta Cryst.* **18**, 62–67.
Coppens, P. & Schmidt, G. M. J. (1965*b*). *Acta Cryst.* **18**, 654–663.
Emsley, J. (1984). *Complex Chemistry, Structure and Bonding*. Vol. 57, pp. 147–191. Berlin: Springer-Verlag.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft University Press.
Moreno-Fuquen, R., De Almeida Santos, R. H. & Lechat, J. R. (1996). *Acta Cryst.* C**52**, 220–222.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Ülkü, D., Huddle, B. P. & Morrow, J. C. (1971). *Acta Cryst.* B27, 432–436.
Zsolnai, L. (1995). *ZORTEP. Interactive Graphics Program.* University of Heidelberg, Germany.

Acta Cryst. (1998). C**54**, 515–517

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

Rodolfo Moreno-Fuquen,[a] Maria Teresa do Prado Gambardella[b] and Jaime Valderrama-N[c]

[a]*Departamento de Química – Facultad de Ciencias, Universidad del Valle, Apartado 25360, Cali, Valle, Colombia,* [b]*DQFM Instituto de Química de São Carlos, USP, CEP 13560.250, São Carlos, SP, Brazil, and* [c]*Departamento de Física – Facultad de Ciencias, Universidad del Valle, Apartado 25360, Cali, Valle, Colombia. E-mail: romoreno@hypatia.univalle.edu.co*

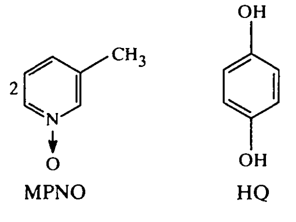
(Received 21 April 1997; accepted 11 November 1997)

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).

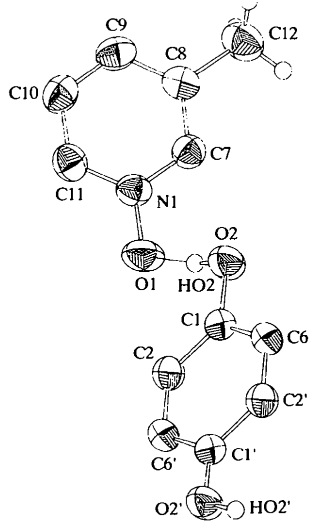


Fig. 1. A perspective view of the title complex with the atomic labelling scheme. Displacement ellipsoids are plotted at the 50% probability level. The ring H atoms have been omitted for clarity.

Acta Crystallographica Section C
ISSN 0108-2701 © 1998