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.
Spek, A. L. (1993). *PLUTON93. Program for the Display and Analysis of Crystal and Molecular Structures.* University of Utrecht, The Netherlands.
Stoe & Cie (1988). *REDU4. Data Reduction Program.* Version 6.2. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1997). C**53**, 1634–1635

The 1:1 Complex Formed by 3-Picoline *N*-Oxide and *p*-Toluic Acid

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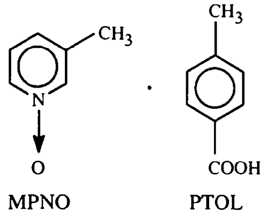
(Received 14 February 1997; accepted 27 May 1997)

Abstract

The title complex, $C_6H_7NO.C_8H_8O_2$, is held together by a hydrogen bond [O···O 2.528 (2) Å] between the carboxyl OH and the O atom of the *N*-oxide. The complex shows a dihedral angle of 33.31 (9)° between the plane of the rings of the molecules.

Comment

The 3-picoline *N*-oxide molecule (MPNO) is an interesting compound and forms molecular complexes with different hydrogen-bond donors. The study of similar molecular complexes has increased in recent years due to the non-linear optical properties that they may exhibit in the solid state (Prasad & Williams, 1991; Moreno-Fuquen, De Almeida Santos & Lechat, 1996, and references therein). In order to complement the crystallographic information and to analyse its behaviour in similar systems, the crystal molecular structure determination of MPNO and *p*-toluic acid (PTOL) was undertaken.



Since satisfactory structural information about MPNO is not available in the literature, other similar systems have been analysed, *e.g.* the picolinic acid *N*-oxide (Laing & Nicholson, 1971). The intramolecular distances and angles of MPNO are in fair agreement with those reported for the picolinic acid *N*-oxide system. The parameter which is affected in the formation of the molecular complex is the C=O bond length of the PTOL molecule which changes from 1.292 (Takwale & Pant, 1971) to 1.206 (2) Å in the present structure. This change may be related to the more accurate values reported in this work. Other intramolecular distances and angles of the PTOL molecule in the present complex appear to be consistent with those reported previously for the free molecule (Takwale & Pant, 1971). An *ORTEP*II (Johnson, 1976) representation of the molecular complex with its numbering scheme is presented in Fig. 1.

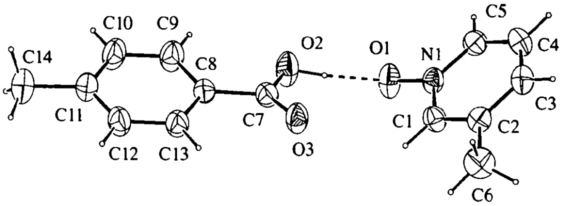


Fig. 1. A perspective view of the molecular complex with the atomic numbering scheme. The displacement ellipsoids are plotted at the 30% probability level.

The title complex owes its formation to an intermolecular hydrogen bond between O2 of the carboxylic group of PTOL and the nitroxide O1 atom of the MPNO molecule. The O···O distance is 2.528 (2) Å and the angle O2—HO2···O1 is 164 (2)°. The dihedral angle formed by the planes of the rings of these molecules is 33.31 (9)°. Formation of infinite chains parallel to the [111] direction was observed. This is due to the occurrence of π–π interactions (Hunter & Sanders, 1990) between the aromatic rings of the molecular complexes related by the centre of inversion (a diagram of this is with the supplementary material). The overlapping rings of the MPNO molecules (symmetry operator $2-x$, $1-y$, $1-z$) have a mean interplanar distance of 3.446 (3) Å and the overlapping rings of the PTOL molecules (symmetry operator $1-x$, $-y$, $-z$) have a mean interplanar distance of 3.288 (8) Å.

Experimental

Crystals of this molecular complex were obtained by slow evaporation from an equimolecular solution of MPNO and PTOL in acetonitrile. Initial reagents were purchased (Aldrich) and were used without additional purification.

Acta Crystallographica Section C
ISSN 0108-2701 © 1997

Crystal data

$C_6H_7NO.C_8H_8O_2$
$M_r = 245.27$
Monoclinic
$P2_1/c$
$a = 13.6819\,(9)$ Å
$b = 7.2379\,(3)$ Å
$c = 14.0407\,(7)$ Å
$\beta = 111.00\,(1)°$
$V = 1298.11\,(12)$ Å^3
$Z = 4$
$D_x = 1.255$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.57–18.16°$
$\mu = 0.089$ mm^{-1}
$T = 295$ K
Transparent prism
$0.18 \times 0.12 \times 0.10$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2740 measured reflections
2629 independent reflections
1844 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.015$
$\theta_{\rm max} = 26.29°$
$h = -17 \rightarrow 0$
$k = 0 \rightarrow 9$
$l = -16 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: 1.13%

Refinement

Refinement on F^2
$R(F) = 0.046$
$wR(F^2) = 0.132$
$S = 1.067$
1844 reflections
169 parameters
H-atom parameters not refined, except for HO2
$w = 1/[\sigma^2(F_o^2) + (0.0813P)^2 + 0.2843P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.005$
$\Delta\rho_{\rm max} = 0.197$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.244$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.015 (3)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

C1—N1	1.346 (2)	C7—O2	1.316 (3)
C2—C6	1.494 (3)	C7—C8	1.486 (3)
N1—O1	1.328 (2)	C11—C14	1.512 (3)
C7—O3	1.206 (2)	O2—H2	0.90 (3)
C3—C2—C6	122.5 (2)	C9—C8—C7	122.2 (2)
C1—C2—C6	119.6 (2)	C13—C8—C7	119.2 (2)
O1—N1—C5	118.8 (2)	C12—C11—C14	121.2 (2)
O3—C7—C8	123.7 (2)	C10—C11—C14	121.1 (2)
O2—C7—C8	113.6 (2)		

The ring H and methyl H atoms were included at geometrically idealized positions. The H2 atom was located from a Fourier difference map and its coordinates were refined. An isotropic displacement parameter of 6.0 Å^2 was assigned to all H atoms.

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 (Sheldrick, 1993). Molecular graphics: *ORTEP*II. Software used to prepare material for publication: *VAXSDP*.

One of the authors (RMF) wants to thank the Brazilian Agency FAPESP for a Postdoctoral Research Fellowship, and FINEP and Universidad del Valle (Colombia) for partial financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1302). Services for accessing these data are described at the back of the journal.

References

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.

Hunter, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Laing, M. & Nicholson, C. (1971). *J. S. Afr. Chem. Inst.* **24**, 186–195.

Moreno-Fuquen, R., De Almeida Santos, R. H. & Lechat, J. R. (1996). *Acta Cryst.* C**52**, 220–222.

Prasad, P. N. & Williams, D. J. (1991). *Introduction to Non-Linear Optical Effects in Molecules and Polymers*, 1st ed. New York: John Wiley.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Takwale, M. G. & Pant, L. M. (1971). *Acta Cryst.* B**27**, 1152–1158.

Acta Cryst. (1997). C**53**, 1635–1637

The 1:1 Complex Formed by 2-Picoline *N*-Oxide and 3-Chlorobenzoic Acid

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(*Received 24 September 1996; accepted 13 May 1997*)

Abstract

The title co-crystal, $C_6H_7NO.C_7H_5ClO_2$, belongs to a series of molecular complexes based on the N—O group and was studied in order to establish its possible non-linear optical behaviour. The 2-picoline *N*-oxide and 3-chlorobenzoic acid moieties are held together by an intermolecular hydrogen bond between the N—O and O—H groups. This system shows a transparency in the visible region of spectra.

Acta Crystallographica Section C
ISSN 0108-2701 © 1997