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1:1 Complex Formed by 2-Picoline *N*-Oxide and 4-Nitrophenol

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Abstract

The 2-picoline *N*-oxide and 4-nitrophenol moieties in the title complex, $C_6H_7NO.C_6H_5NO_3$, are held together by an intermolecular O—H···CN hydrogen bond. This crystal structure exhibits partial overlap between the rings of the molecules, in the [110] direction. The complex formed may be described by two planes which contain the 2-picoline *N*-oxide and 4-nitrophenol molecules, respectively.

Comment

There is a growing interest in the study and development of organic materials that have non-linear properties, as evidenced by the large number of publications on this subject (*e.g.* Pugh, Morley, Nicoud & Twieg, 1987; Prasad & Williams, 1991; Marder, Gorman, Tiemann & Cheng, 1993; Burland, Miller & Walsh, 1994; Kitazawa, Higuchi, Takahashi, Wada & Sasabe, 1995).

The present structure determination is one in a series of investigations of molecular complexes based on 2-picoline *N*-oxide (OPNO). The crystal structure reported in this work is part of an ongoing study into the effect of substitution on the packing of the complexes formed from OPNO and hydrogen-bond donors. The formation of the adduct from OPNO and 4-nitrophenol (PNP) may help to explore the possible applications of this system in non-linear optics. Since the literature does not contain enough structural information about OPNO, other similar systems have been analysed. One structure that could be compared with our system is that of the picolinic acid *N*-oxide (Laing & Nicholson, 1971). The formation of similar adducts from 3-picoline *N*-oxide and fumaric acid, 4-picoline *N*-oxide and 2-nitrobenzoic acid (Gorres, McAfee & Jacobson, 1975; Moreno-Fuquen, de Almeida Santos & Valderrama, 1995) have been undertaken. The N—O bond length of 1.324 (2) Å in the title structure lies between the values of 1.304 (6) Å, found in the adduct of 3-picoline *N*-oxide and fumaric acid, and 1.37 Å in the chlorhydrate of pyridinoxide (Tsoucaris, 1961), and is close to the values reported for picolinic acid *N*-oxide (1.34 Å) and for the adduct of 4-picoline *N*-oxide and 2-nitrobenzoic acid [1.338 (3) Å]. The C—O bond length of 1.364 (3) Å in the present complex is very close to that in the PNP molecule (1.361 Å; Coppens & Schmidt, 1965). Other internal distances and angles of the PNP molecule of the adduct are comparable with those reported for the free molecule, furthermore distances and angles for the pyridinoxide ring are comparable with those reported previously (Laing & Nicholson, 1971; Gorres, McAfee & Jacobson, 1975; Moreno-Fuquen, de Almeida Santos & Valderrama, 1995).
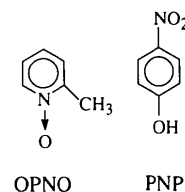
OPNO   PNP

The OPNO + PNP adduct and its numbering scheme are shown in Fig. 1. The molecular complex is held together by an intermolecular hydrogen bond between the O3 of the PNP and the O4 of the *N*-oxide group of the OPNO with an O3···O4 distance equal to 2.600 (3) Å. The dihedral angle formed by the planes which essentially contain the rings of the molecules is 87.75 (8)°. The title complex exhibits overlap between the OPNO and PNP molecules in approximately the [110] direction. The mean interplanar distances between

the overlapped rings are 3.466(5) and 3.40(14) Å. Fig. 2 shows the overlapped molecules along the [110] direction.
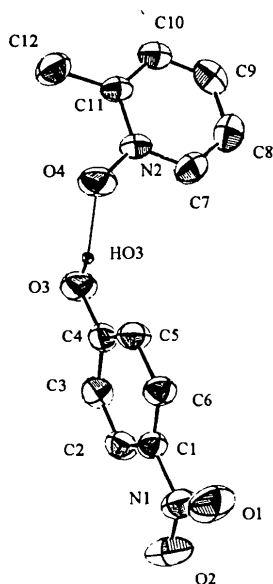

Fig. 1. A displacement ellipsoid representation of the hydrogen-bonded complex showing the atomic numbering. The ellipsoids are drawn at the 50% probability level and the H atoms as spheres of arbitrary radii.
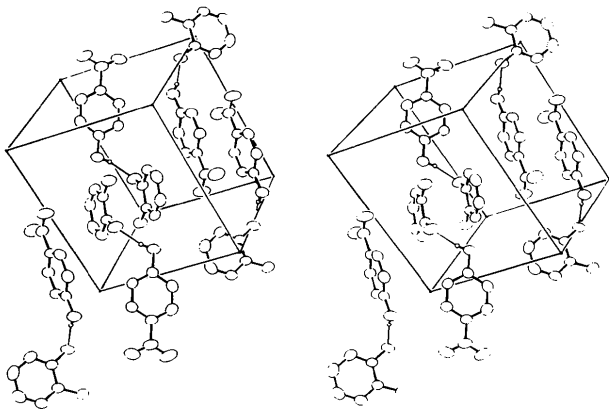

Fig. 2. Stereoscopic view of the molecular packing along the [110] direction.

Experimental

Crystals of the complex were obtained by slow evaporation from an equimolecular solution of the OPNO and PNP in acetonitrile. Regular transparent crystals were obtained with a melting point of 351 (1) K.

Crystal data

$C_6H_7NO.C_6H_5NO_3$
$M_r = 248.24$

Monoclinic
$P2_1/c$
$a = 10.9215 (10)$ Å
$b = 9.540 (2)$ Å
$c = 11.9604 (10)$ Å
$\beta = 107.20 (1)°$
$V = 1190.5 (3)$ Å^3
$Z = 4$
$D_x = 1.385$ Mg m^{-3}

D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.13–18.15°$
$\mu = 0.106$ mm^{-1}
$T = 295$ K
Transparent prism
$0.65 \times 0.35 \times 0.35$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2365 measured reflections
2273 independent reflections
1476 observed reflections [$I > 2.0\sigma(I)$]

$R_{int} = 0.030$
$\theta_{max} = 34.21°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 14$
3 standard reflections frequency: 120 min intensity decay: 1.37%

Refinement

Refinement on F^2
$R(F) = 0.055$
$wR(F^2) = 0.107$
$S = 3.934$
1476 reflections
167 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0092P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.002$

$\Delta\rho_{max} = 0.247$ e Å^{-3}
$\Delta\rho_{min} = -0.232$ e Å^{-3}
Extinction correction: SHELXL93 (Sheldrick, 1993)
Extinction coefficient: 0.0251 (19)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, *Tables 2.2.A*)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.6353 (2)	0.0895 (3)	0.4720 (2)	0.0459 (6)
C2	0.5535 (2)	0.1932 (3)	0.4823 (2)	0.0526 (7)
C3	0.4483 (2)	0.2233 (3)	0.3875 (2)	0.0529 (7)
C4	0.4294 (2)	0.1489 (3)	0.2843 (2)	0.0482 (7)
C5	0.5138 (2)	0.0455 (3)	0.2753 (2)	0.0530 (7)
C6	0.6181 (2)	0.0138 (3)	0.3708 (2)	0.0521 (7)
O1	0.8164 (2)	−0.0406 (2)	0.5638 (2)	0.0880 (7)
O2	0.7664 (2)	0.1316 (3)	0.6586 (2)	0.0872 (8)
O3	0.3250 (2)	0.1825 (2)	0.1930 (2)	0.0664 (6)
N1	0.7474 (2)	0.0574 (3)	0.5724 (2)	0.0613 (7)
C7	0.1904 (2)	−0.1475 (3)	0.0759 (2)	0.0548 (7)
C8	0.0862 (3)	−0.2315 (3)	0.0614 (2)	0.0599 (8)
C9	−0.0133 (2)	−0.2235 (3)	−0.0428 (2)	0.0595 (8)
C10	−0.0027 (2)	−0.1320 (3)	−0.1258 (2)	0.0511 (7)
C11	0.1026 (2)	−0.0477 (3)	−0.1109 (2)	0.0444 (6)
C12	0.1219 (2)	0.0537 (3)	−0.1966 (2)	0.0627 (8)
O4	0.2997 (2)	0.0255 (2)	0.01009 (15)	0.0652 (6)
N2	0.1983 (2)	−0.0571 (2)	−0.0068 (2)	0.0456 (5)

Table 2. *Selected geometric parameters (Å, °)*

C1—C6	1.374 (3)	O2—N1	1.217 (3)
C1—C2	1.362 (3)	C7—N2	1.335 (3)
C1—N1	1.472 (3)	C7—C8	1.360 (3)
C2—C3	1.385 (3)	C8—C9	1.392 (3)

C3—C4	1.385 (3)	C9—C10	1.353 (3)
C4—O3	1.364 (3)	C10—C11	1.371 (3)
C4—C5	1.376 (3)	C11—N2	1.372 (3)
C5—C6	1.387 (3)	C11—C12	1.469 (3)
O1—N1	1.225 (3)	O4—N2	1.324 (2)
C6—C1—C2	122.6 (2)	O1—N1—C1	118.3 (2)
C6—C1—N1	118.3 (2)	N2—C7—C8	121.5 (2)
C2—C1—N1	119.2 (2)	C9—C8—C7	118.9 (3)
C3—C2—C1	119.0 (2)	C10—C9—C8	118.6 (2)
C2—C3—C4	119.5 (2)	C11—C10—C9	122.2 (2)
O3—C4—C5	121.7 (2)	N2—C11—C10	117.7 (2)
O3—C4—C3	117.5 (2)	N2—C11—C12	116.6 (2)
C5—C4—C3	120.7 (2)	C10—C11—C12	125.7 (2)
C6—C5—C4	119.8 (2)	O4—N2—C7	120.4 (2)
C1—C6—C5	118.4 (2)	O4—N2—C11	118.6 (2)
O2—N1—O1	124.1 (2)	C7—N2—C11	121.0 (2)
O2—N1—C1	117.5 (3)		

The ring H atoms were included at geometrically idealized positions with the exception of atom HO3 which was located from a Fourier difference map and its coordinates 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 (Johnson, 1976). Software used to prepare material for publication: *VAXSDP*.

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A Multichromophoric Bicyclo[2.2.2]-octenone and a Photorearranged Ester Derivative

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Abstract

Both the title compound, 5,6-dibenzoyl-4-methoxy-bicyclo[2.2.2]oct-5-en-2-one, $C_{23}H_{20}O_4$, and its photolysis product obtained in the solution phase, 4-methoxy-6-*exo*-methoxycarbonyl-5-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]octan-2-one†, $C_{24}H_{24}O_5$, both crystallize in the monoclinic space group $P2_1/c$. The structures were solved by direct methods. The conformations established for the two compounds facilitate understanding of the mechanism of the photoreaction in solution.

Comment

UV irradiation of a solution of 5,6-dibenzoyl-4-methoxybicyclo[2.2.2]oct-5-en-2-one, (I), in methanol gave the ester 4-methoxy-6-*exo*-methoxycarbonyl-5-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]octan-2-one, (II), *via* a ketene intermediate formed by a 1,5-phenyl migration in compound (I) (Lahiri & Singh, 1989). The ^{1}H NMR spectrum of compound (II) showed a highly shielded δ value (2.55 p.p.m.) for the methoxy bridge-

† IUPAC name: methyl 4-methoxy-2-oxo-5-(1-phenoxy-1-phenyl-methylene)bicyclo[2.2.2]octanyl-6-*exo*-carboxylate.