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# 1:1 Complex of 2,4-dinitrophenol and 4-methoxypyridine *N*-oxide hydrate

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**Key indicators**

Single-crystal X-ray study
*T* = 293 K
Mean σ(C–C) = 0.003 Å
*R* factor = 0.045
*wR* factor = 0.132
Data-to-parameter ratio = 10.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.



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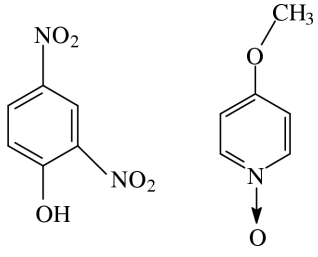
The title cocrystal, $C_6H_7N_1O_2{\cdot}C_6H_4N_2O_5$, owes its formation to an intermolecular hydrogen bond between the O—H and N—O groups [O···O 2.461 (2) Å]. The angle between the planes of the rings of the molecules is 88.82 (7)°. The crystal structure exhibits overlap between the rings of the molecules in the [102] direction. The rings are stacked in the crystal, with a mean interplanar distance of 3.318 (2) Å.

## Comment

Continuing an ongoing study of the properties of molecular complexes formed from various pyridine *N*-oxide derivatives and several hydrogen-bond donors, and particularly to complement the crystallographic information available on compounds based on 4-methoxypyridine *N*-oxide (MEPNO), to analyse the type of hydrogen-bond in the title complex and to study its non-linear optical properties, the crystal structure determination of MEPNO and 2,4-dinitrophenol (DNP) was undertaken.




DNP MEPNO

The title complex is the first organic molecular complex with MEPNO as a precursor. Other series of molecular complexes with nitropyridine *N*-oxide as a precursor have been reported (Moreno-Fuquen *et al.*, 2000). The crystal structure of free MEPNO has not been reported. Several organometallic structures where MEPNO forms diverse complexes are reported in the literature. From the Cambridge Structural Database (CSD; Allen *et al.*, 1991), the molecular parameters of three structures, namely, bis(4-methoxypyridine *N*-oxide)dichlorocopper (CSD refcode PIJDUH; Le Fur *et al.*, 1993), trifluorobis(4-methoxypyridine *N*-oxide)antimony(III) hydrate (FMXPSB; Dewan *et al.*, 1975) and free 2,4-dinitrophenol (DNOPHL01; Iwasaki & Kawano, 1977), may be used as a reference to analyse the behaviour of the present complex. A displacement ellipsoid plot of the hydrogen-bonded complex with the atomic numbering scheme is shown in Fig. 1.

In the title complex, the DNP and MEPNO molecules are held together by a strong intermolecular hydrogen bond

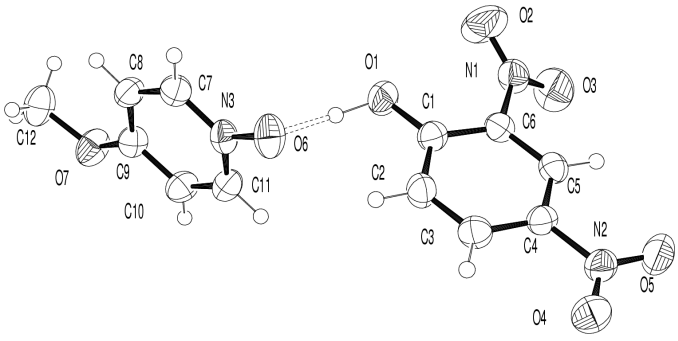



**Figure 1**
A perspective *ORTEP*-3 (Farrugia, 1997) view of the title molecular complex with the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

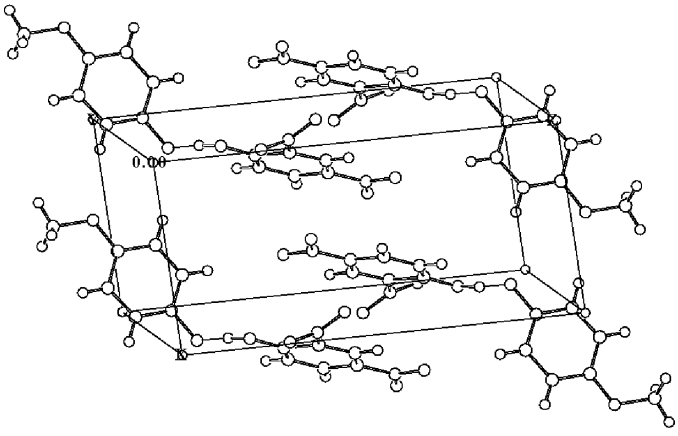



**Figure 2**
A *ZORTEP* (Zsolnai, 1995) plot of the packing showing the overlapped rings along the [102] direction.

(Emsley, 1984) between the O1 atom of the phenol group of the DNP molecule and nitroxide O6 atom of the MEPNO molecule. The O1···O6 distance is 2.461 (2) Å and the O1–HO1...O6 angle is 175 (3)°. The O1–HO1 and HO1...O6 distances are 1.01 (4) and 1.45 (4) Å, respectively. If one compares the molecular parameters of the title complex with those of PIJDUH, FMXPSB and DNOPHL01, the C7—C8 bond length changes from 1.371 (3) Å in the title system to 1.395 (9) Å in MSXPSB, and the C9—C10 bond length changes from 1.387 (3) Å in the title complex to 1.412 (8) Å in PIJDUH. The C1—O1 and C4—N2 bond lengths change from 1.319 (2) and 1.454 (2) Å, respectively, in the title complex to 1.343 (5) and 1.484 (3) Å in DNOPHL01. The other bond lengths and angles agree well with those reported for PIJDUH, FMXPSB and DNOPHL01. A dihedral angle of 88.82 (7)° formed by the least-squares planes containing the phenyl rings of MEPNO and DNP is shown by the title complex. The nitro O5—N2—O4 and O2—N1—O3 groups form dihedral angles of 2.06 (4) and 35.71 (3)°, respectively, with the DNP ring. The pyridine ring is planar, with the C12 and O6 atoms lying 0.082 (1) and 0.071 (1) Å out of this plane; these distances are similar to those reported for the pyridine N-oxide ligand (Horrocks *et al.*, 1968). The crystal structure exhibits overlap between the rings of the molecules in the [102] direction. The molecules of the title complex are overlapped in the crystal with the MEPNO ring at a mean interplanar distance of 3.318 (2) Å from the other MEPNO ring at $-x, 1-y, 1-z$. The presence of a centre of symmetry in the crystal inhibits the SHG response.

## Experimental

Single crystals suitable for X-ray analysis were obtained by slow evaporation from an equimolecular solution of DNP and MEPNO in acetonitrile. Pale-yellow transparent prisms were obtained with a melting point of 418 (1)K.

*Crystal data*

$C_6H_7NO_2{\cdot}C_6H_4N_2O_5$
$M_r = 309.24$
Triclinic, $P\overline{1}$
$a = 6.7683$ (5) Å
$b = 7.4976$ (7) Å
$c = 14.4864$ (2) Å
$\alpha = 87.92$ (1)°
$\beta = 90.77$ (1)°
$\gamma = 114.18$ (1)°
$V = 670.19$ (8) Å$^3$
$Z = 2$
$D_x = 1.532$ Mg m$^{-3}$
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2.0$–35.0°
$\mu = 1.11$ mm$^{-1}$
$T = 293$ (2) K
Transparent prism, pale yellow
0.22 × 0.16 × 0.15 mm

*Data collection*

Seifert diffractometer
$\omega/2\theta$ scans
2329 measured reflections
2229 independent reflections
2060 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 66.7°$
$h = -7 \rightarrow 7$
$k = -8 \rightarrow 8$
$l = 0 \rightarrow 16$
2 standard reflections
every 150 reflections
intensity decay: 2.0%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.132$
$S = 1.14$
2229 reflections
215 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 0.3304P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.45$ e Å$^{-3}$
$\Delta\rho_{min} = -0.29$ e Å$^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.029 (2)

**Table 1**
Hydrogen-bonding geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—HO1···O6 | 1.01 (4) | 1.45 (4) | 2.461 (2) | 175 (3) |

The ring and methyl H atoms were added at calculated positions. The H atoms were treated with a riding model with *SHELXL*97 (Sheldrick, 1997) defaults (C—H = 0.93–0.97 Å) and were not refined. The HO1 atom was found from a difference map and its coordinates were refined.

Data collection: *Crysom Diffraction Software* (Seifert, 1995); cell refinement: *Crysom Diffractometer Software*; data reduction: *Crysom Diffractometer Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *ZORTEP* (Zsolnai, 1995); software used to prepare material for publication: *SHELXL*97.

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