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The 1:1 complex of 3,5-dinitrobenzoic acid and 4-methylpyridine *N*-oxide

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Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.002 Å
R factor = 0.035
wR factor = 0.095
Data-to-parameter ratio = 14.0

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

In the title co-crystal, $C_7H_4N_2O_6 \cdot C_6H_7NO$, the two components are linked by an intermolecular hydrogen bond between the O—H and N—O groups [O···O 2.487 (1) Å]. The dihedral angle formed by the planes of the rings of the component molecules is 7.40 (7)°. The rings of the complex are stacked along the *b* axis of the crystal. The stacks exhibit overlap between the aromatic rings, with a mean interplanar distance of 3.136 (1) Å.

Comment

The *para*-methylpyridine *N*-oxide molecule (PPNO) represents an interesting system which tends to form molecular complexes with diverse hydrogen-bond donors (Moreno-Fuquen *et al.*, 1995). The synthesis and characterization of the title PPNO and 3,5-dinitrobenzoic acid (DNBA) complex, (I), have a twofold purpose: (*a*) to enrich the crystallographic information on compounds based on PPNO and (*b*) to analyse the type of hydrogen bonding in the title complex, (I).

PPNO   DNBA
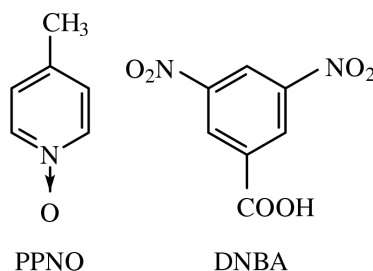
(I)

The DNBA–PPNO adduct with the adopted atom-numbering scheme is shown in Fig. 1. The molecular complex owes its formation to a strong hydrogen bond (Emsley, 1984) between the O7 atom of the *N*-oxide group of PPNO and the O3 atom of the DNBA carboxylic group. The O7···O3 distance is 2.487 (1) Å and the angle O7···HO3–O3 is 176 (2)°. The O3—HO3 and O7···HO3 distances are 0.95 (2) and 1.54 (2) Å, respectively. The dihedral angle formed by the planes of the rings of the component molecules is 7.40 (7)°.

The structure of the pyridine oxide component is close to that found in a number of structures involving pyridine oxide derivatives, *e.g.* 4-methylpyridine *N*-oxide [Morris *et al.*, 1998; Cambridge Structural Database (Allen *et al.*, 1991) refcode NUSCAF], 4,4′-dimethyl-2,2′-bipyridine 1,1′-dioxide (Kanno & Iijima, 1997; TUDREP), 3,5-dinitrobenzoic acid (Domenicano *et al.*, 1990; CUKCAM10) and 3-methyl-nitropyridine-1-oxide 3,5-dinitrobenzoic acid (Bochuan *et al.*, 1995; FAFTAH). The N3—O7 bond length changes from
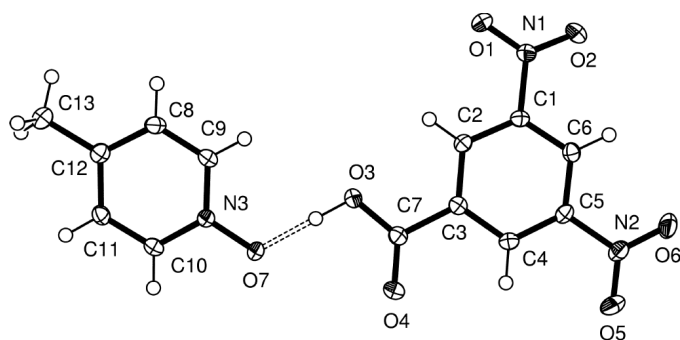
Figure 1
An *ORTEP*-3 (Farrugia, 1997) plot of the asymmetric unit of (I) showing the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as spheres of an arbitrary radii.

1.3335 (12) Å in (I) to 1.309 and 1.301 Å, respectively, in the NUSCAF and TUDREP structures. The C3—C7, O4—C7 and O3—C7 bond lengths in the CUKCAM10 structure change from 1.4837 (8), 1.2357 (7) and 1.2844 (5) Å to 1.5062 (15), 1.2187 (14) and 1.3074 (14) Å, respectively, in the title complex. The latter changes in bond lengths may be explained by the formation of the intermolecular hydrogen bond in the title complex. The structure of the DNBA moiety in the title complex is very similar to that of the same moiety in the FAFTAH structure.

The rings of the complex are stacked in the crystal along the *b* axis (Fig. 2). The resulting stacks exhibit overlap between the aromatic rings with a mean interplanar distance of 3.136 (1) Å.

Experimental

Crystals of (I) were obtained from a mixture of equimolecular solutions of PPNO and DNBA in acetonitrile, which was left to evaporate slowly. Initial reagents were purchased from Aldrich and were used without additional purification. The melting point of the crystals of (I) is 403 (1) K.
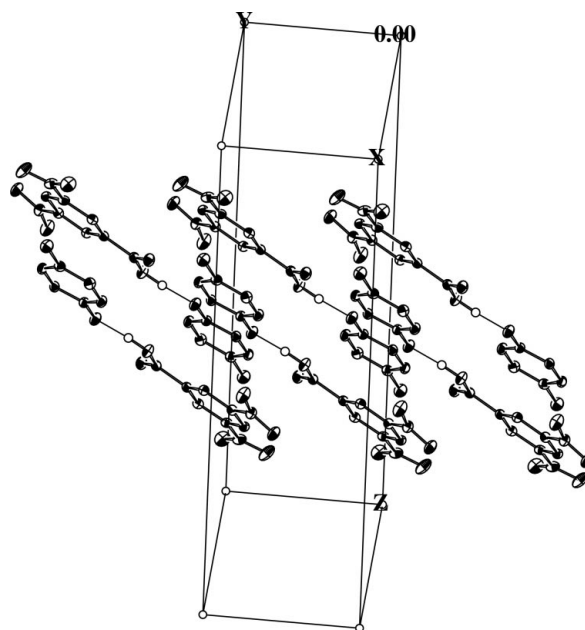

Figure 2
A ZORTEP view (Zsolnai, 1995) of the crystal packing showing the overlapped rings along the *b* axis.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$+ 0.05663P]$,
$wR(F^2) = 0.095$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
2973 reflections	$\Delta\rho_{max} = 0.31$ e Å^{-3}
212 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

C2—C3	1.3948 (15)	C7—O3	1.3074 (14)
C3—C4	1.393 (2)	C9—N3	1.3518 (14)
C3—C7	1.5062 (15)	C10—N3	1.3531 (14)
C7—O4	1.2187 (14)	N3—O7	1.3335 (12)
C4—C3—C7	118.13 (10)	O3—C7—C3	113.21 (9)
C2—C3—C7	121.49 (10)	O7—N3—C9	121.12 (9)
O4—C7—O3	125.76 (10)	O7—N3—C10	117.91 (9)
C4—C3—C7—O4	−1.5 (2)	C4—C5—N2—O5	7.8 (2)
C6—C1—N1—O2	9.7 (2)		

All H atoms, with the exception of the carboxylic acid atom HO3, were placed in geometrically calculated positions and included in the refinement as riding. The displacement parameters of the H atoms were given a value of 1.2U_{eq}, where U_{eq} is the equivalent displacement parameter of the carrier atom. The HO3 atom was located in a difference Fourier synthesis and refined isotropically.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Enraf–Nonius, 1989); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*86 (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.

Crystal data

C$_7$H$_4$N$_2$O$_6$·C$_6$H$_7$NO
$M_r = 321.25$
Monoclinic, $P2_1/n$
$a = 9.2223$ (2) Å
$b = 6.3266$ (1) Å
$c = 23.4991$ (4) Å
$\beta = 93.6067$ (7)°
$V = 1368.36$ (4) Å^3
$Z = 4$
$D_x = 1.559$ Mg m^{-3}
$D_m = 1.547$ Mg m^{-3}

D_m measured by flotation in KI solution
Mo $K\alpha$ radiation
Cell parameters from 2643 reflections
$\theta = 1.0–27.5°$
$\mu = 0.13$ mm^{-1}
$T = 123$ K
Cut plate, yellow
$0.20 \times 0.15 \times 0.08$ mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: none
4607 measured reflections
2973 independent reflections
2759 reflections with $I > 2\sigma(I)$

$R_{int} = 0.011$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 11$
$k = -7 \rightarrow 8$
$l = -30 \rightarrow 30$

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References

Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.

Bochuan, D., Wenyu, P., Tongde, X., Jiangzhong, C. & Songxian, L. (1995). *Fuzhou Dax Xuebao, Zir. Kex. (J. Fuz University Nat. Sci.)*, **23**, 89.

Domenicano, A., Schultz, G., Hargittai, I., Colapietro, M., Portalone, G., George, P. & Bock, C. W. (1990). *Struct. Chem.* **1**, 107–122.

Emsley, J. (1984). *Complex Chemistry, Structure and Bonding*. Vol. 57, pp. 147–191. Berlin: Springer-Verlag.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Kanno, H. & Iijima, K. (1997). *Acta Cryst.* C**53**, 498–499.

Moreno-Fuquen, R., Valderrama-N., J., Abboud, K. A. & Strouse, C. (1995). *Annais Assoc. Bras. Quim.* **44**, Part 3, 34–41.

Morris, E. K., Cousson, A. & Paulus, W. (1998). *Z. Kristallogr. New Cryst. Struct.* **213**, 80.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter and R. M. Sweet, pp. 307–326. London: Academic Press.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Zsolnai, L. (1995). *ZORTEP*. University of Heidelberg, Germany.