The 1:1 Complex Formed by 4-Nitropyridine *N*-Oxide and 4-Aminobenzoic Acid

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Abstract

The co-crystal, $C_5H_4N_2O_3.C_7H_7NO_2$, owes its formation to an intermolecular hydrogen bond between the N—O and O—H groups. The crystal structure exhibits overlap between the rings of the molecules in the [110] direction. There is no short nitroamino intermolecular distance.

Comment

This work is part of a series of structural studies on the 4-nitropyridine *N*-oxide (NPNO) derivatives. At the moment two derivatives of NPNO and aminobenzoic acids are known: NPNO + 2-aminobenzoic acid (OABA; Moreno Fuquen, Lechat & de Almeida Santos, 1991) and NPNO + 3-aminobenzoic acid (MABA; Moreno Fuquen, de Castro & Lechat, 1992). The crystal structure determination of NPNO + 4-aminobenzoic acid (PABA) has been undertaken in order to analyse the type of hydrogen bond formed, to prove the existence of other intermolecular contacts and to explore the possibility of application of this system in non-linear optics.
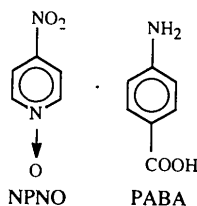
NPNO   PABA

Fig. 1 illustrates the NPNO and PABA adduct as a whole. This molecular complex owes its formation to an intermolecular hydrogen bond between O1 of the *N*-oxide group of NPNO and O—H of the carboxyl group of PABA. The O1···O5 distance is 2.640 (4) Å. There is another weaker intermolecular hydrogen bond between HN32 and O4 (symmetry $\frac{1}{2} - x, 2 - y, z - \frac{1}{2}$). This

links molecules in chains along the *c* axis. Additional hydrogen-bond information is given in Table 3. This molecular complex exhibits overlap between NPNO and PABA molecules in the [110] direction. The mean interplanar distance between the overlapped rings are equal to 3.48 (4) and 3.50 (4) Å. Fig. 2 shows two symmetry-related molecules which form the half of the cell contents growing in the *c* direction. This molecular complex may be described by two planes, which essentially contain the rings of both molecules with a dihedral angle equal to 127.65 (8)°. The internal distances and angles of the NPNO and PABA moieties are consistent with the data reported in the literature (Eichhorn, 1956; Wang, Blessing, Ross & Coppens, 1976; Lai & Marsh, 1967). There is a difference in the C6—C7 distance in PABA, changing from 1.455 (6) and 1.464 (6) to 1.485 (5) Å. This difference is attributed to the hydrogen-bond formation of the molecular complex.
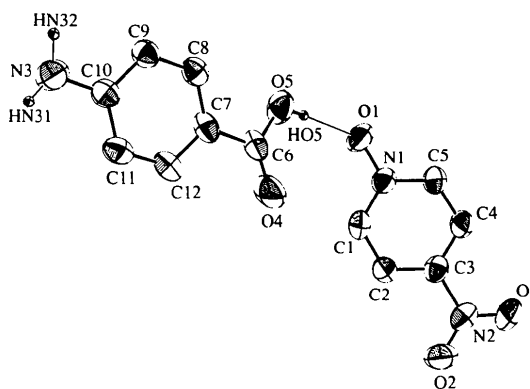

Fig. 1. Representation of the hydrogen-bonded complex showing the atomic numbering. The displacement ellipsoids are shown at the 50% probability level.
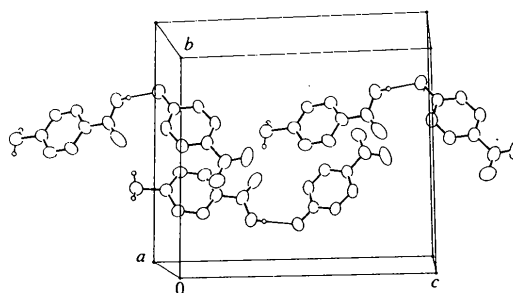

Fig. 2. The molecular packing shows a system formed by chains extended along the *c* axis and linked by hydrogen bonds.

As has been observed for other NPNO-aminobenzoic systems (NPNO–OABA, NPNO–MABA), this system does not have the nitroaniline interactions (see Table 3). This is contrary to the observations in nitroaniline systems (Panunto, Urbánczyk-Lipkowska, Johnson & Etter, 1987; Etter, 1990). The second harmonic generation of this compound is poor because of an absorption band in the UV–visible region.

† In memoriam.

Experimental

The co-crystal can be obtained by two methods: by a solid-state reaction and from solution. The solid-state reaction involves mixing finely ground powders of the starting materials in an agate mortar: a colour change from yellow to orange-red is seen. The crystal used for this structure determination was prepared by slow evaporation from an equimolar solution of the starting compounds in acetonitrile.

Crystal data

$C_5H_4N_2O_3.C_7H_7NO_2$	Mo $K\alpha$ radiation
$M_r = 277.24$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
$a = 7.0549\,(10)$ Å	$\theta = 10.46–18.47°$
$b = 12.4741\,(10)$ Å	$\mu = 0.117$ mm^{-1}
$c = 14.1928\,(10)$ Å	$T = 295$ K
$V = 1249.0\,(2)$ Å^3	Prism
$Z = 4$	$0.2 \times 0.2 \times 0.1$ mm
$D_x = 1.474$ Mg m^{-3}	Red-orange
$D_m = 1.45$ Mg m^{-3}	
D_m measured by flotation, KI solution	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.029$
$\omega/2\theta$ scans	$\theta_{max} = 26.31°$
Absorption correction: none	$h = 0 \rightarrow 8$
	$k = 0 \rightarrow 15$
1504 measured reflections	$l = 0 \rightarrow 17$
1479 independent reflections	3 standard reflections
1191 observed reflections	frequency: 120 min
$[I > 2.0\sigma(I)]$	intensity decay: 1.9%

Refinement

Refinement on F^2	Extinction correction:
$R(F) = 0.0448$	*SHELXL93* (Sheldrick,
$wR(F^2) = 0.1134$	1993)
$S = 1.796$	Extinction coefficient:
1479 reflections	0.065 (8)
182 parameters	Atomic scattering factors
H-atom parameters not refined	from *International Tables for X-ray Crystallography*
$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2]$	(1974, Vol. IV)
where $P = (F_o^2 + 2F_c^2)/3$	Absolute configuration:
$(\Delta/\sigma)_{max} < 0.001$	Flack (1983)
$\Delta\rho_{max} = 0.205$ e Å^{-3}	
$\Delta\rho_{min} = -0.209$ e Å^{-3}	

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

U_{iso} for H atoms, $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	*y*	*z*	U_{eq}/U_{iso}
N1	0.0529 (5)	0.6907 (2)	0.4733 (2)	0.0522 (7)
O1	0.0426 (5)	0.7686 (2)	0.5344 (2)	0.0749 (8)
C1	-0.0145 (5)	0.7068 (3)	0.3848 (2)	0.0555 (9)
C2	0.0019 (5)	0.6289 (3)	0.3175 (2)	0.0535 (8)
C3	0.0846 (4)	0.5340 (3)	0.3418 (2)	0.0458 (7)
C4	0.1489 (5)	0.5163 (3)	0.4321 (2)	0.0538 (8)
C5	0.1319 (5)	0.5963 (3)	0.4961 (2)	0.0573 (9)
N2	0.1044 (4)	0.4490 (3)	0.2713 (2)	0.0598 (8)
O2	0.0660 (6)	0.4712 (3)	0.1898 (2)	0.0928 (10)
O3	0.1601 (5)	0.3617 (2)	0.2966 (2)	0.0776 (8)
C6	0.0884 (5)	1.1547 (3)	0.7571 (2)	0.0585 (9)
C7	0.1536 (4)	1.1481 (3)	0.6578 (2)	0.0490 (8)
C8	0.2383 (4)	1.2345 (3)	0.6128 (2)	0.0504 (8)
C9	0.2964 (5)	1.2254 (2)	0.5197 (2)	0.0482 (8)
C10	0.2678 (5)	1.1309 (2)	0.4694 (2)	0.0485 (8)
C11	0.1823 (5)	1.0447 (2)	0.5159 (2)	0.0529 (8)
C12	0.1293 (5)	1.0530 (3)	0.6082 (3)	0.0543 (8)
N3	0.3177 (5)	1.1251 (2)	0.3759 (2)	0.0628 (8)
O4	0.0404 (5)	1.0772 (2)	0.8025 (2)	0.0890 (10)
O5	0.0784 (5)	1.2532 (2)	0.7901 (2)	0.0723 (8)
HO5	0.0431	1.2594	0.8396	0.076
HN31	0.4225	1.1778	0.3595	0.076
HN32	0.3281	1.0595	0.3494	0.076

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

N1—O1	1.305 (3)	C6—O4	1.210 (4)
N1—C5	1.342 (4)	C6—O5	1.316 (4)
N1—C1	1.358 (4)	C6—C7	1.485 (5)
C1—C2	1.367 (5)	C7—C12	1.389 (5)
C2—C3	1.363 (5)	C7—C8	1.389 (4)
C3—C4	1.378 (4)	C8—C9	1.388 (5)
C3—N2	1.464 (4)	C9—C10	1.393 (4)
C4—C5	1.354 (4)	C10—N3	1.375 (4)
N2—O3	1.212 (4)	C10—C11	1.399 (4)
N2—O2	1.220 (4)	C11—C12	1.366 (5)
O1—N1—C5	121.1 (3)	O4—C6—O5	122.7 (3)
O1—N1—C1	119.0 (3)	O4—C6—C7	123.2 (3)
C5—N1—C1	119.9 (3)	O5—C6—C7	114.0 (3)
N1—C1—C2	120.7 (3)	C12—C7—C8	118.8 (3)
C3—C2—C1	118.5 (3)	C12—C7—C6	119.4 (3)
C2—C3—C4	121.0 (3)	C8—C7—C6	121.8 (3)
C2—C3—N2	119.8 (3)	C9—C8—C7	120.1 (3)
C4—C3—N2	119.2 (3)	C8—C9—C10	121.0 (3)
C5—C4—C3	118.5 (3)	N3—C10—C9	120.2 (3)
N1—C5—C4	121.4 (3)	N3—C10—C11	121.7 (3)
O3—N2—O2	123.8 (3)	C9—C10—C11	118.1 (3)
O3—N2—C3	118.7 (3)	C12—C11—C10	120.8 (3)
O2—N2—C3	117.5 (3)	C11—C12—C7	121.2 (3)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—HO5$\cdots$O1^i	0.749 (3)	1.891 (3)	2.640 (4)	177.4 (3)
N3—HN32$\cdots$O4^{ii}	0.904 (3)	2.053 (3)	2.909 (4)	157.5 (3)
N3—HN31$\cdots$O3^{iii}	1.016 (3)	3.080 (3)	3.349 (4)	96.4 (2)

Symmetry codes: (i) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $\frac{1}{2} - x, 2 - y, z - \frac{1}{2}$; (iii) $x, 1 + y, z$.

The H ring atoms were included at geometrically idealized positions. The HO5 atom was found from a difference map and its coordinates were fixed. An isotropic temperature factor 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: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *VAXSDP*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1177). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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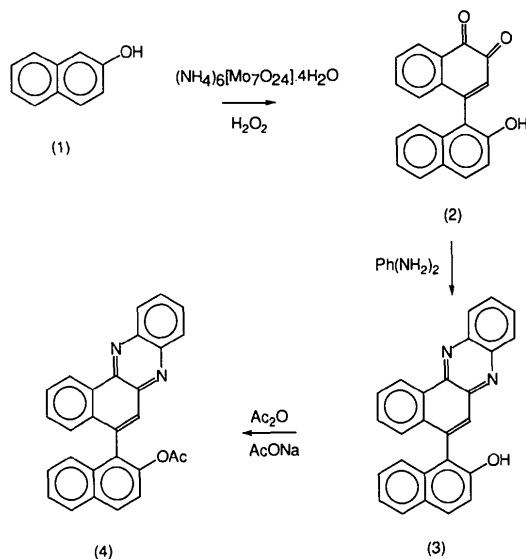Wang, Y., Blessing, R. H., Ross, F. K. & Coppens, P. (1976). *Acta Cryst.* **B32**, 572–578.

Fig. 1. As expected, both the benzo[a]phenazin-5-yl and naphthyl ring systems are planar (r.m.s. deviations 0.028 and 0.015 Å, respectively). The mean planes of the two ring systems are inclined at 80.42 (7)° and the normal to the plane of the acetate group forms an angle of 76.6 (1)° with that of the naphthyl ring. None of the

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1-(Benzo[a]phenazin-5-yl)-2-acetyloxy-naphthalene,† $C_{28}H_{18}N_2O_2$

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Abstract

The angle between the benzo[a]phenazin-5-yl and naphthyl rings is 80.42 (7)° and the benzo[a]phenazin-5-yl rings exhibit π–π stacking.

Comment

The title compound, (4), has been prepared previously (Bader, 1951) but the structure has not been reported. A perspective view of a molecule of (4) is shown in

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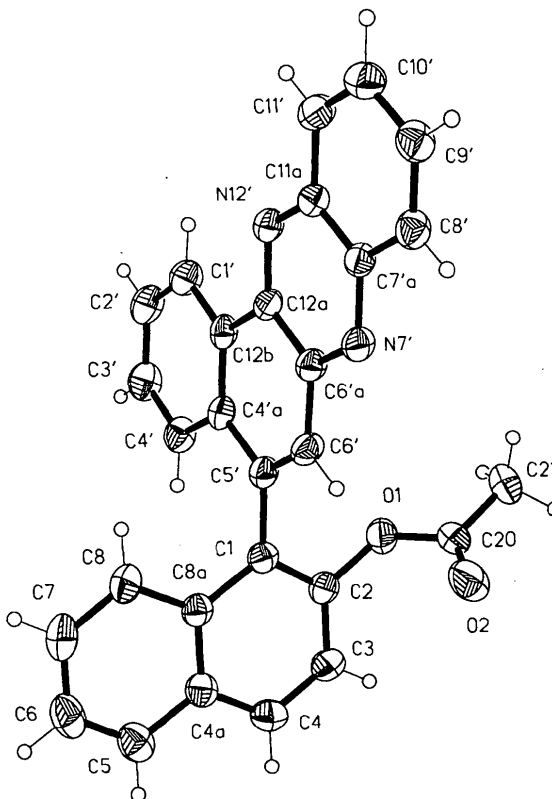† Alternative nomenclature: 1-(benzo[a]phenazin-5-yl)naphthalen-2-yl acetate.

Fig. 1. Perspective views of the title molecule showing 30% probability displacement ellipsoids. The H atoms are shown as small spheres for clarity.