

The 2:1 complex of 4-aminobenzoic acid and 4,4'-bipyridyl *N,N'*-dioxideRodolfo Moreno-Fuquen,^{a*}
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Key indicators

Single-crystal X-ray study

 $T = 293\text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$ R factor = 0.044 wR factor = 0.146

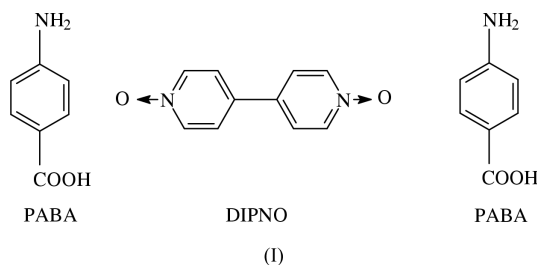
Data-to-parameter ratio = 21.2

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

The co-crystal $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2 \cdot 2\text{C}_7\text{H}_7\text{NO}_2$ owes its formation to an intermolecular hydrogen bond between the O—H and N—O groups; the O...O distance is 2.5796 (17) Å. The dihedral angle between the planes of the pyridyl *N*-oxide and aminobenzoic rings of the complex is 10.2 (1)°. An additional intermolecular C—H...O hydrogen bond is formed, giving rise to an eight-membered ring within the asymmetric unit. The structure is centrosymmetric about the mid-point of the bond joining the two pyridine rings. The crystal structure exhibits overlap between the aromatic rings of the molecules in the $[\bar{1}10]$ direction.

Comment

The title compound, (I), was investigated as part of a study on $D-\text{H} \cdots A$ hydrogen bonding in systems containing 4,4'-bipyridyl *N,N'*-dioxide and hydrogen-bond donors (Thaimattam *et al.*, 1998). Four molecular structures similar to (I) were found in the Cambridge Structural Database (Allen, 2002), namely 4,4'-bipyridine *N,N'*-dioxide urea clathrate, 4,4'-bipyridine *N,N'*-dioxide thiourea clathrate and 4,4'-bipyridine *N,N'*-dioxide dihydrate clathrate (Thaimattam *et al.*, 1998), and 4-aminobenzoic acid (Lai & Marsh, 1967); they were used as reference standards in analysing the structural characteristics of complex (I).



The complex is held together by a strong intermolecular hydrogen bond (Emsley, 1984) between the O—H group of the 4-aminobenzoic acid (PABA) molecule and the N—O group of the 4,4'-bipyridyl *N,N'*-dioxide (DIPNO) molecule. In the crystal structure, two acid components, related by a centre of symmetry, are linked to a centrosymmetric 4,4'-bipyridyl *N,N'*-dioxide, not only by short O—H...O bonds but also by longer C5—H5...O3 hydrogen bonds, giving rise to an eight-membered ring within the asymmetric unit. This results in an approximately linear chain of the three molecules. The formation of these hydrogen bonds is probably related to the rotation of the carboxylic acid group around the C9—C12 bond [the dihedral angle between this group and the C6—C11

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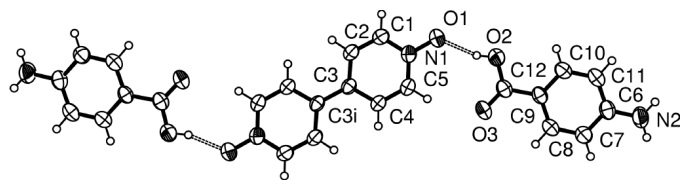


Figure 1
An ORTEP-3 (Farrugia, 1997) plot of the title complex, with the atomic labelling scheme. Displacement ellipsoids are plotted at the 50% probability level. H atoms are shown as spheres of arbitrary radius.

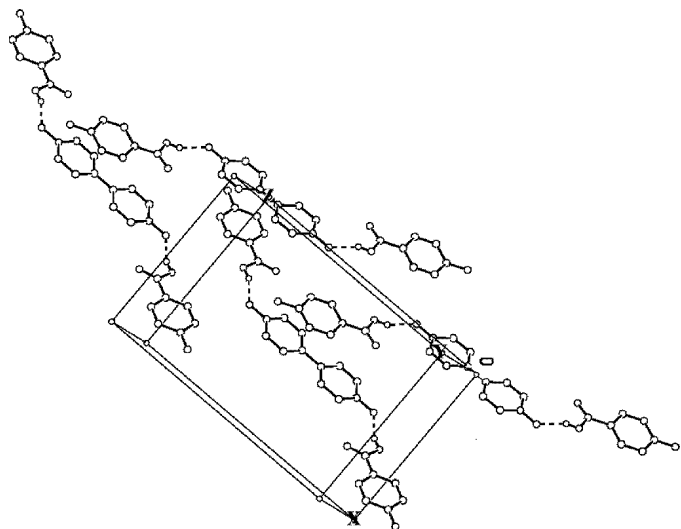


Figure 2
A ZORTEP (Zsolnai, 1995) diagram of (I), showing the overlap between the molecules along the $[110]$ direction.

ring being $7.5(1)^\circ$] and to the approximate planarity of the whole centrosymmetric unit. Hydrogen-bond $\text{O}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ interactions are presented in Table 2. A perspective view of the DIPNO–PABA (1:2) adduct, showing the atomic numbering scheme, is given in Fig. 1. The dihedral angle formed by the planes which contain the rings of the DIPNO and PABA molecules is $10.2(1)^\circ$. The values of bond lengths and other internal parameters of DIPNO are very close to values reported in the literature (Thaimattam *et al.*, 1998). The central $\text{C}3-\text{C}3^i$ bond length [$1.475(3) \text{ \AA}$; symmetry code: (i) $-x, -y, -z$] is shorter than a normal $\text{C}-\text{C}$ single-bond distance, showing that this $\text{C}-\text{C}$ bond probably has a little π -bond character. The presence of a strong $\text{O}-\text{H}\cdots\text{O}$ and other relatively weak $\text{C}-\text{H}\cdots\text{O}$ intermolecular hydrogen bonds induces some structural changes in the donor complex. Indeed, the $\text{C}9-\text{C}12$, $\text{C}12-\text{O}2$ and $\text{C}12-\text{O}3$ bond lengths change from $1.471(2)$, $1.320(2)$ and $1.218(2) \text{ \AA}$ in (I) to $1.455(4)$, $1.295(3)$ and $1.248(5) \text{ \AA}$ in the uncomplexed PABA molecule. There are no unusual short intermolecular contacts in the crystal structure. The molecules of PABA and DIPNO ($\frac{1}{2} - x, -y, z - \frac{1}{2}$) overlap along the $[\bar{1}10]$ direction at a distance of $3.454(2) \text{ \AA}$ (Fig. 2). Additionally, hydrogen-bond interactions between atom $\text{N}2$ with atoms $\text{O}3^{ii}$ and $\text{O}1^{iii}$ of neighboring molecules [symmetry codes: (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$] are observed (Fig. 3).

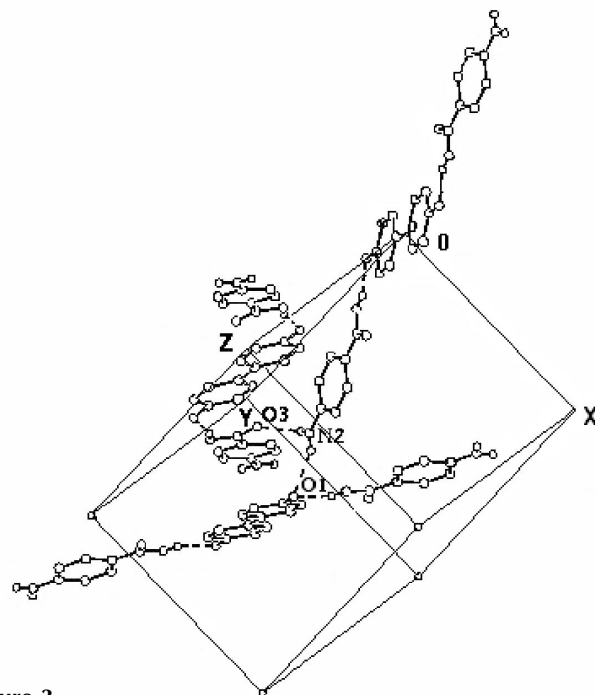


Figure 3
A ZORTEP (Zsolnai, 1995) view of (I), showing additional hydrogen bonds, indicated by dashed lines.

Experimental

Yellow single crystals of DIPNO–PABA (1:2) [m.p. $453(1) \text{ K}$] suitable for X-ray analysis were obtained by slow evaporation from an equimolar solution of DIPNO and PABA in methanol. Initial reagents were purchased from Aldrich and were used without additional purification.

Crystal data

$\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2 \cdot 2\text{C}_7\text{H}_7\text{NO}_2$
 $M_r = 462.46$
 Orthorhombic, *Pbca*
 $a = 11.188(1) \text{ \AA}$
 $b = 12.138(2) \text{ \AA}$
 $c = 16.354(2) \text{ \AA}$
 $V = 2220.9(5) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.383 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 9-18^\circ$
 $\mu = 0.10 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Regular block, yellow
 $0.22 \times 0.18 \times 0.12 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 6757 measured reflections
 3350 independent reflections
 2057 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

$\theta_{\text{max}} = 30.4^\circ$
 $h = 0 \rightarrow 15$
 $k = 0 \rightarrow 17$
 $l = -23 \rightarrow 23$
 3 standard reflections
 frequency: 120 min
 intensity decay: 1.9%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.146$
 $S = 1.02$
 3350 reflections
 158 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0639P)^2 + 0.5535P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$

Table 1
Selected geometric parameters (Å, °).

O1—N1	1.3243 (16)	C3—C3 ⁱ	1.475 (3)
O1—N1—C1	119.23 (13)	O3—C12—O2	122.43 (15)
O1—N1—C5	120.95 (13)	O3—C12—C9	123.00 (15)
N2—C6—C7	120.26 (16)	O2—C12—C9	114.53 (13)
C8—C9—C12—O2	174.67 (14)		

Symmetry code: (i) $-x, -y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—HO2 \cdots O1	0.90 (2)	1.73 (2)	2.580 (2)	157 (2)
N2—HN21 \cdots O3 ⁱⁱ	0.86	2.23	2.975 (2)	146
N2—HN22 \cdots O1 ⁱⁱⁱ	0.86	2.30	3.095 (2)	154
C5—H5 \cdots O3	0.93	2.39	3.273 (2)	158

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

All H atoms, with the exception of the carboxyl atom HO2, were placed at geometrically idealized positions and were allowed to ride on their parent atoms; N—H = 0.86, C—H = 0.93 Å and $U_{iso}(H) =$

$1.2U_{eq}$ of the carrier atom. Hydroxyl atom HO2 was located from a Fourier difference map and its coordinates were refined freely.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *ZORTEP* (Zsolnai, 1995); software used to prepare material for publication: *SHELXL97*.

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