

The 1:1 adduct of 4-aminobenzoic acid with 4-aminobenzonitrile

Graham Smith,^{a*} Raymond C. Bott^a and Daniel E. Lynch^b

^aCentre for Instrumental and Developmental Chemistry, Queensland University of Technology, GPO Box 2434, Brisbane 4001, Australia, and ^bSchool of Natural and Environmental Sciences, Coventry University, Coventry CV1 5FB, England
Correspondence e-mail: g.smith@qut.edu.au

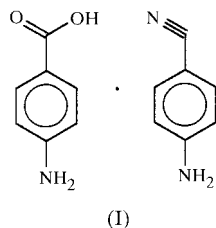
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The 1:1 adduct of 4-aminobenzoic acid (PABA) with 4-aminobenzonitrile (PABN), $C_7H_7NO_2 \cdot C_7H_6N_2$, consists of a primary centrosymmetric cyclic hydrogen-bonded PABA dimer interaction [$O \cdots O$ 2.640 (3) Å] peripherally linked into chains by weaker hydrogen bonds *via* a head-to-tail PABN interaction [$N \cdots N$ 3.179 (4) and $N \cdots O$ 3.062 (4) Å], and is linked between the chains by amine-N (PABN) to amine-N (PABA) interactions [$N \cdots N$ 3.233 (5) Å]. No proton transfer occurs.

Comment

4-Aminobenzoic acid (PABA) is an important biological molecule, being an essential bacterial cofactor involved in the synthesis of folic acid (Robinson, 1966), as well as acting as an antagonist to the action of the drug sulfonamide in competition for essential growth metabolites (Pauling & Hayward, 1964). As a simple organic molecule which promotes the extension of hydrogen-bonded network structures it has no equal, having associations with neutral molecules such as 4-nitropyridine *N*-oxide (Lechat, 1984), 1,3,5-trinitrobenzene (Lynch *et al.*, 1994) and urea (Smith, Baldry *et al.*, 1997), with Lewis bases such as 4-(4-nitrobenzyl)pyridine (Smith, Lynch *et al.*, 1997), and with carboxylic acids such as 2,4,6-trinitrobenzoic acid (Lynch *et al.*, 1992*a*), (2,4-dichlorophenoxy)acetic acid (Lynch *et al.*, 1992*b*), 2-(carboxyphenoxy)acetic acid (Byriel *et al.*, 1991) and 3,5-dinitrosalicylic acid (Smith *et al.*, 1995).



The ability of strong carboxylic acids to protonate the amine group of PABA often results in the formation of acid–

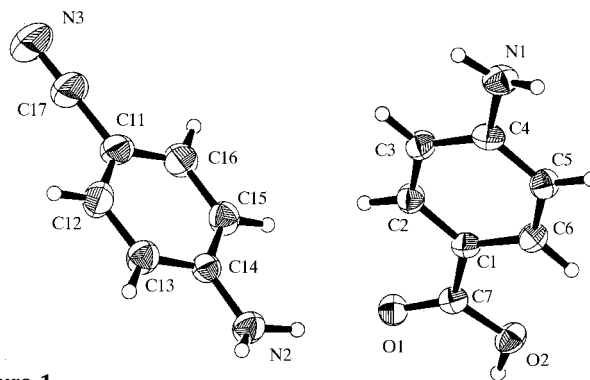


Figure 1

The molecular configuration of adduct (I) and the atom-numbering scheme, showing 30% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

(PABA)₂ associations in which one PABA is protonated while the second is not. This is found in the adduct with 3,5-dinitrosalicylic acid. In a review of the adducts of PABA (Smith, Lynch *et al.*, 1997), the most common primary associative mode was recognized as the *A–A* homodimer, in which the two PABA molecules form a cyclic hydrogen-bonded dimer [graph set $R_2^2(8)$; Etter, 1990], such as is found in the parent acid (Lai & Marsh, 1967) and in the adduct with (2,4-dichlorophenoxy)acetic acid. The less common form is the *A–B* [$R_2^2(8)$] heterodimer, which is found with the (2-carboxyphenoxy)acetic acid adduct.

Our previous work has involved the adducts of PABA with carboxylic acids and with Lewis bases, and was extended in the present study to include 4-aminobenzonitrile (PABN), a

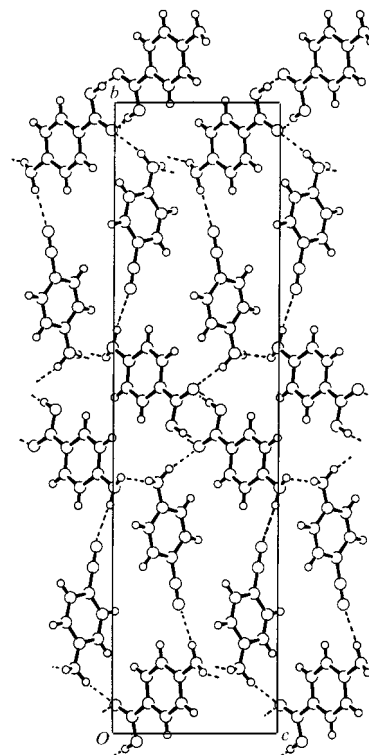


Figure 2

The packing in the unit cell of (I) viewed down the *a* axis, showing the hydrogen-bonding interactions as broken lines.

molecule not unlike PABA, having potential for hydrogen-bonding extension *via* the cyanide group. We present here the crystal structure analysis of the 1:1 PABA–PABN adduct, (I).

In adduct (I), the PABA molecules form the common primary *A–A* cyclic hydrogen-bonded dimers across crystallographic inversion centres [O2–HO2··O1(1 – *x*, –*y*, –*z*) 2.640 (3) Å and 173 (3)°]. Weaker secondary interactions link these dimer units along the *b* direction (Fig. 2) through both the cyanide and amino groups of the PABN molecule [N1–H10··N3(–1 + *x*, ½ – *y*, ½ + *z*) 3.179 (5) Å and 164 (3)°; N2–H20··O1 3.062 (4) Å and 159 (3)°]. These chains are held together by lateral hydrogen bonds between the PABA and PABN amine groups [N1–H11··N2(–1 + *x*, *y*, 1 + *z*) 3.233 (5) Å and 139 (3)°].

Experimental

The synthesis of (I) was carried out by refluxing equimolar (2 mmol) amounts of 4-aminobenzoic acid and 4-aminobenzonitrile for 15 min at *ca* 350 K in 95% ethanol (20 ml). Crystals of (I) were obtained after evaporation of the solvent at room temperature.

Crystal data

C₇H₇NO₂·C₇H₆N₂
M_r = 255.28
 Monoclinic, *P*2₁/*c*
a = 4.860 (3) Å
b = 32.543 (4) Å
c = 8.538 (3) Å
 β = 94.79 (4)°
V = 1345.6 (8) Å³
Z = 4

D_x = 1.260 Mg m^{–3}
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 10–20°
 μ = 0.087 mm^{–1}
T = 153 K
 Prismatic, colourless
 0.3 × 0.2 × 0.2 mm

Data collection

Rigaku AFC-7R diffractometer
 ω scans with profile analysis
 2723 measured reflections
 2372 independent reflections
 1614 reflections with *I* > 1.5σ(*I*)
*R*_{int} = 0.074
 θ_{\max} = 25°

h = 0 → 5
k = 0 → 38
l = –10 → 10
 3 standard reflections
 frequency: 150 min
 intensity decay: none

Table 1

Selected geometric parameters (Å, °).

O1–C7	1.240 (3)	N2–C14	1.368 (4)
O2–C7	1.319 (3)	N3–C17	1.127 (4)
N1–C4	1.379 (4)		
C2–C1–C7	119.3 (3)	O2–C7–C1	115.1 (3)
C6–C1–C7	122.1 (3)	C12–C11–C17	119.5 (4)
N1–C4–C3	120.5 (3)	C16–C11–C17	121.6 (4)
N1–C4–C5	121.0 (3)	N2–C14–C13	121.2 (3)
O1–C7–O2	122.1 (3)	N2–C14–C15	120.5 (3)
O1–C7–C1	122.7 (3)	N3–C17–C11	179.5 (6)

Refinement

Refinement on *F*
R = 0.045
wR = 0.043
S = 1.795
 1614 reflections
 193 parameters
 H atoms treated by a mixture of independent and constrained refinement

(Δ/σ)_{max} = 0.002
 $\Delta\rho_{\max}$ = 0.14 e Å^{–3}
 $\Delta\rho_{\min}$ = –0.16 e Å^{–3}
 Extinction correction: Zachariasen (1968) type 2 Gaussian isotropic
 Extinction coefficient: 8.001

The parameters of the H atoms involved in hydrogen bonding were refined (HO2, H11, H12, H21 and H22). All other H atoms were allowed for as riding.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structure: *SIR88* (Burla *et al.*, 1989); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1290). Services for accessing these data are described at the back of the journal.

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