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Redetermination of the β-polymorph of *p*-aminobenzoic acid

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.003 Å
R factor = 0.050
wR factor = 0.131
Data-to-parameter ratio = 15.5

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

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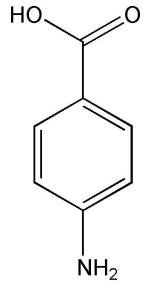
Single crystals of *p*-aminobenzoic acid, $C_7H_7NO_2$, were grown from water. In the structure, there is one molecule of the acid present in the asymmetric unit. Hydrogen bonds between adjacent molecules lead to the formation of a three-dimensional network.

Comment

p-Aminobenzoic acid (PABA) is used primarily in making pharmaceuticals. Other uses include perfumes, dyes and feedstock additives. The substance has been a model compound in our extensive study of controlled crystallization of polymorphs, where the thermodynamic stability and crystallization from different solvents have been studied extensively (Gracin & Rasmuson, 2004).



(I)

The crystal structure of the β-polymorph of PABA has been determined previously (Alleaume *et al.*, 1966). However, the precision of this structure determination was limited and the positions of the H atoms were not determined. In order to be able to study hydrogen bonding in this compound, we decided to redetermine this structure. It should be mentioned that there are reports of several other modifications of PABA, one of which, the α form, was characterized by single-crystal X-ray diffraction (Lai & Marsh, 1967). In addition, PABA readily forms cocrystals with suitable compounds. The crystal structures of many of these adducts have been characterized; for two recent examples, see Lynch & McClenaghan (2001) and Moreno-Fuquen *et al.* (2003).

In this structural form of PABA, there is one molecule of the acid present in the asymmetric unit. The geometry of the acid molecule, which is shown in Fig. 1, is unexceptional. Each of these acid molecules is bonded to three other molecules *via* hydrogen bonds in a fashion that is shown in Fig. 2. The hydrogen bonds involve the OH group and one of the NH H atoms as donors. The lone pair of the NH_2 group and of the carboxy O atom function as acceptors. This pattern of hydrogen bonds yields the three-dimensional network shown

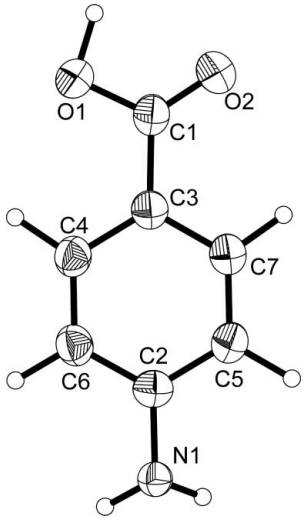


Figure 1
The molecule of *p*-aminobenzoic acid. Displacement ellipsoids are drawn at the 50% probability level.

in Fig. 2. This structure is thus clearly quite different from that of the other monoclinic modification (the α form), where there are two molecules in the asymmetric unit and discrete dimers are formed *via* hydrogen bonding between two carboxy groups.

Experimental

Crystals were grown from aqueous solutions that were obtained by dissolving the purchased material (Sigma–Aldrich, >99% purity) in pure distilled and de-ionized water at 293 K. The clear solutions were slowly evaporated to dryness for a couple of weeks. The rate of evaporation was adjusted by covering the solution with perforated Para-film. Crystals with two different habits, needles and prisms, were obtained concomitantly in this experiment. The crystal structure determination described here was carried out on a prismatic crystal.

Crystal data

$C_7H_7NO_2$
M_r = 137.14
Monoclinic, $P2_1/n$
a = 6.2782 (3) Å
b = 8.5831 (4) Å
c = 12.3649 (6) Å
β = 100.133 (2)°
V = 655.91 (5) Å^3
Z = 4
D_x = 1.389 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3547 reflections
θ = 4.1–26.4°
μ = 0.10 mm^{-1}
T = 298 K
Prism, colourless
0.30 × 0.15 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: none
6455 measured reflections
1329 independent reflections
897 reflections with $I > 2\sigma(I)$
R_{int} = 0.061
θ_{max} = 26.4°
$h = -7 \rightarrow 7$
$k = -10 \rightarrow 9$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.131
S = 1.03
1329 reflections
86 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 0.2521P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

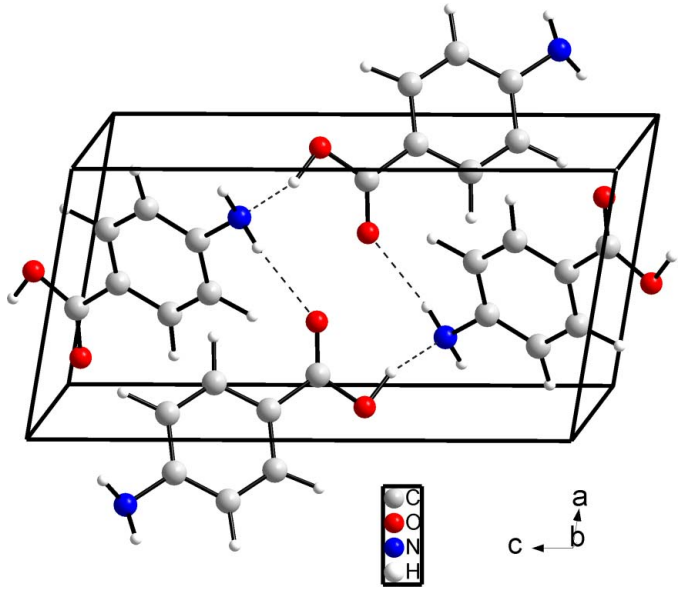


Figure 2
A packing diagram of *p*-aminobenzoic acid, showing the unit cell and the network formed by hydrogen-bonded acid molecules.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1^{i}	1.07	1.73	2.754 (2)	160
N1—H1A···O2^{ii}	0.88	2.19	3.045 (2)	164

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

All H atoms were located in a difference Fourier map and were refined using a riding model in their as-found relative positions, with C—H distances in the range 1.07–1.12 Å and N—H distances of 0.88 and 0.96 Å, and with the constraint U_{iso}(H) = 1.2U_{eq}(carrier atoms) applied in all cases.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *MAXUS* (Mackay *et al.*, 1999).

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References

Alleaume, M., Salas-Cimingo, G. & Decap, J. (1966). *C. R. Acad. Sci. Ser. C*, **262**, 416–417.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Brandenburg, K. (1999). *DIAMOND*. Release 2.1e. Crystal Impact GbR, Bonn, Germany.
Gracin, S. & Rasmuson, Å. (2004). *Cryst. Growth Des.* **4**, 1013–1023.
Lai, T. F. & Marsh, R. E. (1967). *Acta Cryst.* **22**, 885–893.
Lynch, D. E. & McClenaghan, I. (2001). *Acta Cryst.* C**57**, 830–832.
Mackay, S., Gilmore, C. J., Edwards, C., Stewart, N. & Shankland, K. (1999). *MAXUS*. Bruker Nonius, The Netherlands, MacScience, Japan and The University of Glasgow, Scotland.

Moreno-Fuquen, R., Font i Carot, M., Garriga, M., Cano, F., Martinez-Ripoll, M., Valderrama-Naranjo, J. & Serratto, L. M. (2003). *Acta Cryst.* E**59**, o495–o497.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.