No further crystallographic work on this complex is contemplated.

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Twinning in p-aminobenzoic acid. By R. C. G. KILLEAN, *Physics Department, St.Salvator's College, St. Andrews, Scotland,* P. TOLLIN, *Physics Department, Queen's College, Dundee, Scotland,* D. G. WATSON*, *Department of Chemistry, The University, Glasgow, Scotland,* and D. W. YOUNG, *Physics Department, Queen's College, Dundee, Scotland*

p-Aminobenzoic acid is a growth factor for several micro-organisms. Its presence enables the organisms to synthesize the more complex molecule of vitamin Bc.

Groth (1908) has quoted that crystals of p-aminobenzoic acid belong to the monoclinic prismatic class with axial ratios $1\cdot4403:1:0\cdot7312, \beta = 100° 10'$ and density $1\cdot393$ g.cm^{-3} at 20°C. This observation was verified by Prasad, Kapadia & Thakar (1937) who published unit-cell dimensions $a = 12\cdot26, b = 8\cdot61, c = 6\cdot30$ Å, $\beta = 100° 10'$, which gave axial ratios $1\cdot424:1:0\cdot732$ and calculated density $1\cdot38$ g.cm^{-3}. Prasad et al. mention crystallization difficulties and indicate that the crystals were rhombic plates obtained by repeated slow crystallization from aqueous alcohol. The present authors have attempted to repeat this work with the purpose of verifying that p-aminobenzoic acid molecules associate as dimers. Recrystallization of commercially available p-aminobenzoic acid from the solvents listed in Table 1 gave three distinct crystallographic forms. Despite repeated re-crystallization the rhombic plate modification has not been obtained.

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From the approximate nature of the *mmm* symmetry, the C-face centring that is indicated, and the fact that the systematic absences do not conform to any space group, it is deduced that all three modifications are twins. In addition many of the photographs of the upper levels of form I showed streaks attributed to disorder, although the streaks never appeared on photographs of the *hk*0 reflexions. Careful examination indicated that physical separation of the twins appeared unlikely and that the crystals are probably polysynthetic twins. Under these circumstances one is forced to work with the twinned material, and indeed, a trial structure was obtained for the (001) projection of form I before general data were collected and it was realized that the crystal was twinned.

The (001) projection of form I, which has *mm* symmetry and apparent axes of $12\cdot75$ Å and $13\cdot58$ Å has pseudo *pgg* plane space group, there being a few relatively weak axial reflexions having $h = 2n + 1$ and one exceptionally weak $k = 2n + 1$ which cannot be explained as Renninger reflexions. The trial structure was obtained by computing an $(E^2 - 1)$ Patterson function for the (001) projection with the data collected by the multiple-film Weissenberg technique. The presence of a benzene ring was immediately obvious and

Table 1. *Crystallographic modifications of p-aminobenzoic acid*

Solvent	Morphological habit	Crystal-lographic modification	Symmetry class of reciprocal space	Axial lengths (Å)			Comments
				a	b	c	
Anhydrous ethanol Aqueous ethanol Methanol Water Acetone Ether and petroleum spirit Acetone and water Acetone acid	Acicular and fibrous / Blades and fibrous Spherolitic	I	Approximately *mmm*	25·50	27·16	3·85	White crystals which become straw coloured on exposure to the atmosphere.
Dioxan	(a) Prismatic	II	Approximately *mmm*	43·88	12·00	20·68	Straw coloured rapidly decomposing to white powder unless sealed in glass tube. II and III have different systematic absences.
	(b) Bladed	III	Approximately *mmm*	43·88	12·00	20·68	

it was positioned in real space by obtaining the best fit to the axial reflexions, assuming *pgg* symmetry. A structure-factor calculation based on this benzene ring, followed by an electron-density map, yielded the positions of the remaining atoms. Further Fourier and least-squares refinement reduced the reliability index, defined as $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$, from 0·37 to 0·12. Postulation of probable hydrogen positions reduced the reliability index to 0·10. The coordinates obtained at this stage are given in Table 2; the corresponding electron-density map (Fig. 1) gives clear verification that *p*-aminobenzoic acid molecules are associated as dimeric pairs.

On the basis of being able to obtain a structure and consideration of the density and unit-cell parameters it can be assumed that the twinning is such that the single-crystal constituents have identical rectangular projections down the twin *c* axis. The departure from *mmm* symmetry in the upper layer lines was attributed to each portion of the twin being present in differing amounts, and to the possible
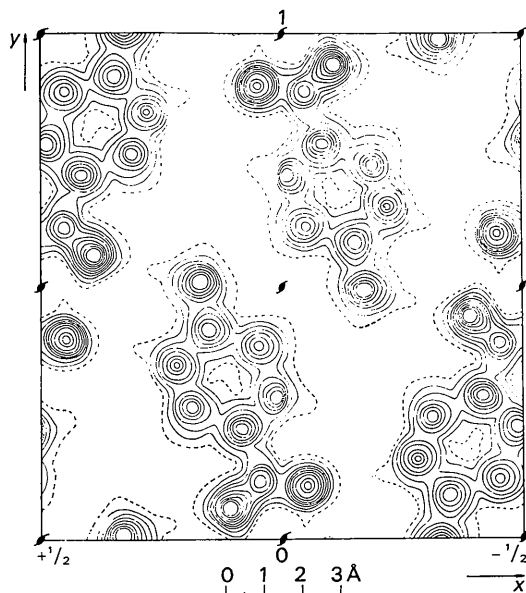
Table 2. *Atomic coordinates and isotropic temperature factors*

Atom	x/a	y/b	$B(\text{Å}^{-2})$
C(1)	+0·147	+0·416	3·9
C(2)	+0·218	+0·351	3·9
C(3)	+0·186	+0·256	4·2
C(4)	+0·083	+0·226	3·7
C(5)	+0·013	+0·286	4·4
C(6)	+0·043	+0·384	3·9
C(7)	+0·051	+0·124	4·2
N(8)	+0·177	+0·513	4·1
O(9)	+0·109	+0·066	3·9
O(10)	−0·050	+0·102	3·9

monoclinic symmetry of the single crystallites, although on consideration of the unit-cell dimensions alone it is difficult to see how this could be the monoclinic form reported by Prasad *et al.* If the crystallites are monoclinic then this is an example of a crystal showing para-orthorhombic symmetry of the type discussed by Dunitz (1964).

Clearly under certain favourable conditions it is possible to elucidate details of a crystal structure with the use of a twinned crystal, but the fact of obtaining a rectangular projection with *mm* symmetry by no means guarantees that Fourier techniques can be applied to obtain a solution. If it is assumed that twinning is on a gross enough scale, then the intensities which arise at superimposed reciprocal lattice points will be proportional to the sum of the squares of the structure factors for each reciprocal lattice point. If the twinning is not on such a gross scale the relative phases of the structure factors will be important. Thus care must be exercised in applying the usual Fourier methods of crystal determination. In this case with the twinned crystal data available it is impossible to determine the *x* coordinates of the atoms in form I without recourse to an image seeking technique in Patterson space.

No further work is contemplated on the twinned crystals unless a single crystal is obtained.

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Fig. 1. Electron density projection perpendicular to *c* of form I. The contours are at intervals of 1 e.Å⁻²: the 1 e.Å⁻² contour is shown dashed.

The growth of crystals in silica gel, and the unit-cell dimensions of cadmium oxalate and copper tartrate.

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It has been known for at least fifty years that single crystals of some insoluble compounds can be grown by allowing suitable ions to diffuse slowly together in a suitable medium where they react. Johnson (1914) allowed the reactants to diffuse into a large volume of water and obtained crystals

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of calcium hydroxide, while Hatschek (1911) prepared small crystals of gypsum by allowing sulphate ions to diffuse into a gelatin gel which had been prepared from a dilute solution of calcium chloride. Dreaper (1913) obtained crystals of lead chloride by using a glass capillary tube, sealed at one end, to contain one of the reacting solutions and placing the other, open, end of the tube into a solution of the other reactant. Holmes (1917) has briefly reviewed previous work on crystallization in various media, including agar and gel-