water molecules are each involved in such linkages with two different complex molecules, and as well form donor linkages to a carbonyl O of two further complex molecules. Each complex molecule is thus involved in eight extramolecular hydrogen bonds, the carbonyl O atoms each being involved in one intra- and one intermolecular bond.

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The Monoclinic Form of *p*-Hydroxyacetanilide

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Abstract. HO–$C_6H_4NHCOCH_3$, m.p. 168–170°C, monoclinic, $P2_1/a$, a = 12·93 (4), b = 9·40 (1), c = 7·10 (2) Å, β = 115·9 (2)°. D_m = 1·30, D_x = 1·296 g cm^{-3}, Z = 4. The structure was refined to R = 0·072 for 1382 non-zero reflexions. The molecules are linked together by two kinds of hydrogen bonds [2·663 (3) Å, OH donates to O=C; 2·934 (3) Å, OH accepts from H–N] to form a pleated sheet parallel to the *ac* plane and the sheets are stacked along **b**. The dihedral angle between the benzene ring and the amide group is 21·2°. The structure is compared with that of the orthorhombic form.

Introduction. The monoclinic crystals obtained from an aqueous solution were prisms elongated along **c**. Intensity data were collected on Weissenberg photographs with specimens 0·3 × 0·3 × 0·6 mm for the layers *hk*0 to *hk*5, and 0·4 × 0·6 × 0·2 mm for the layers *h*0*l* to *h*7*l*. Visually estimated intensities were corrected for Lorentz and polarization factors and for spot shape, but no absorption correction was made [μ(Cu $K\alpha$) = 8·0 cm^{-1}].

Intensities of 1382 non-zero reflexions (78% of the reflexions within Cu $K\alpha$ sphere) were placed on an approximately absolute scale by a Wilson plot (B = 3·19 Å^2).

The structure was solved from a Patterson map. Block-diagonal least-squares refinement reduced R from 0·35 to 0·11. A difference Fourier synthesis revealed the H atoms except for those of the methyl group. Further refinement including the H atoms reduced R to 0·092. After correction for extinction for the six strongest reflexions, a difference Fourier synthesis revealed all the H atoms. Refinement including all the atoms gave a final R value of 0·072 for 1382 non-zero reflexions.* The weights adopted were w = 1·0 for $0 < |F_o| \leq 7·0$ and $w = (7·0/|F_o|)^2$ for $|F_o| > 7·0$. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The computations were performed on an NEAC 2200-500 computer at the Okayama University Computer Center. The programs used were *HBLS*-5 and *DAPH* (Ashida, 1973).

Table 1. *The final positional and thermal parameters* (× 10^4) *with standard deviations in parentheses*

The anisotropic temperature factors have the form exp $[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	2228 (2)	851 (2)	560 (3)	70 (1)	138 (3)	233 (5)	72 (3)	151 (4)	94 (6)
O(2)	−1923 (2)	4977 (2)	−5458 (3)	69 (1)	168 (3)	170 (4)	3 (3)	83 (4)	47 (6)
N	−1599 (2)	4436 (2)	−2145 (3)	52 (1)	86 (2)	173 (5)	4 (3)	84 (4)	17 (5)
C(1)	−611 (2)	3547 (2)	−1519 (3)	44 (1)	68 (2)	164 (5)	−16 (3)	58 (4)	−9 (5)
C(2)	142 (2)	3562 (2)	−2442 (4)	57 (2)	82 (3)	178 (5)	−15 (3)	91 (5)	21 (6)
C(3)	1089 (2)	2656 (3)	−1721 (4)	56 (2)	101 (3)	206 (6)	−9 (4)	131 (5)	−2 (7)
C(4)	1290 (2)	1740 (3)	−69 (4)	51 (2)	86 (3)	183 (5)	−4 (3)	92 (5)	−13 (6)
C(5)	551 (2)	1744 (3)	887 (4)	62 (2)	103 (3)	215 (6)	21 (4)	116 (6)	90 (7)
C(6)	−387 (2)	2641 (3)	160 (4)	55 (2)	106 (3)	216 (6)	9 (4)	126 (5)	59 (7)
C(7)	−2196 (2)	5067 (2)	−4003 (4)	55 (2)	79 (3)	163 (5)	−23 (3)	58 (5)	1 (6)
C(8)	−3233 (3)	5896 (3)	−4176 (4)	75 (2)	119 (3)	233 (7)	46 (5)	66 (6)	33 (8)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31567 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *The final parameters of the hydrogen atoms*

	x	y	z	B (Å^2)
H(1)	0·001 (3)	0·421 (3)	−0·351 (5)	2·2 (0·6)
H(2)	0·165 (2)	0·272 (3)	−0·230 (4)	1·1 (0·5)
H(3)	0·070 (3)	0·113 (3)	0·204 (5)	2·0 (0·6)
H(4)	−0·091 (3)	0·264 (3)	0·079 (5)	2·7 (0·7)
H(5)	0·239 (3)	0·055 (4)	0·184 (5)	2·9 (0·7)
H(6)	−0·193 (3)	0·451 (3)	−0·126 (5)	2·0 (0·6)
H(7)	−0·382 (4)	0·583 (5)	−0·556 (7)	6·0 (1·1)
H(8)	−0·328 (4)	0·593 (4)	−0·298 (6)	4·9 (0·9)
H(9)	−0·306 (4)	0·701 (6)	−0·422 (7)	7·2 (1·2)

Table 3. *The least-squares planes and displacements of the atoms from the planes, in the monoclinic and orthorhombic forms*

(M) and (O) refer to the monoclinic and orthorhombic forms, respectively. $X=ax+cz\cos\beta$, $Y=by$, $Z=cz\sin\beta$ for (M).

(I) Benzene ring

(M): $-0{\cdot}3036X-0{\cdot}7066Y-0{\cdot}6391Z+1{\cdot}6485=0$
(O): $0{\cdot}4283X-0{\cdot}2340Y-0{\cdot}8728Z+0{\cdot}9963=0$

	Shift (Å) (M)	Shift (Å) (O)		Shift (Å) (M)	Shift (Å) (O)
C(1)*	0·010	0·016	C(8)	0·313	0·112
C(2)*	−0·007	−0·012	H(1)	−0·05	−0·03
C(3)*	−0·002	−0·005	H(2)	−0·08	−0·02
C(4)*	0·008	0·018	H(3)	−0·02	−0·04
C(5)*	−0·005	−0·011	H(4)	−0·00	−0·06
C(6)*	−0·004	−0·007	H(5)	−0·23	0·36
O(1)	0·032	0·060	H(6)	−0·20	0·33
O(2)	0·811	−0·492	H(7)	1·02	−0·03
N	0·003	0·111	H(8)	−0·07	−0·32
C(7)	0·402	−0·126	H(9)	−0·48	1·05

(II) Amide group

(M): $-0{\cdot}4677X-0{\cdot}8194Y-0{\cdot}3315Z+2{\cdot}3070=0$
(O): $0{\cdot}1579X-0{\cdot}1341Y-0{\cdot}9783Z+2{\cdot}0730=0$

O(2)*	0·0002	0·0014	C(1)	0·046	0·022
N*	0·0002	0·0012	C(2)	−0·360	0·395
C(7)*	−0·0005	−0·0037	C(6)	0·497	−0·316
C(8)*	0·0002	0·0010	H(1)	−0·70	0·59

(III) Six-membered ring formed by C(1), N, C(7), O(2), H(1) and C(2)

(M): $-0{\cdot}2554X-0{\cdot}8807Y-0{\cdot}3989Z+2{\cdot}6682=0$
(O): $0{\cdot}3358X-0{\cdot}1045Y-0{\cdot}9361Z+0{\cdot}7519=0$

C(1)*	0·201	−0·100	O(2)*	0·141	−0·160
N*	−0·100	0·064	H(1)*	−0·20	0·16
C(7)*	−0·099	0·036	C(2)*	0·101	0·023

Dihedral angles (°) between the planes

	(I) and (II)	(I) and (III)
(M)	21·1	17·3
(O)	17·7	9·8

* Atoms used in the calculation of the planes.

The final atomic parameters are listed in Tables 1 and 2. Bond lengths and angles are shown in Fig. 1. The projection of the crystal structure viewed down **b** is shown in Fig. 2. The displacements of the atoms from the least-squares planes are listed in Table 3, together with those of the orthorhombic form.

Discussion. In order to compare the stacking mode of the dimorphs of *p*-hydroxyacetanilide, the structure of the monoclinic form has been determined as an extension of the previous work on the orthorhombic form (Haisa, Kashino & Maeda, 1974).

The molecular geometry is closely similar to that of the orthorhombic form; in both forms the C(4)–O(1) bond length agrees well with that expected for $pK_a=10$ (Andersen & Andersen, 1975) and the C(1)–N, N–C(7) and C(7)–O(2) lengths are close to the respective average lengths in planar anilides. The benzene rings take

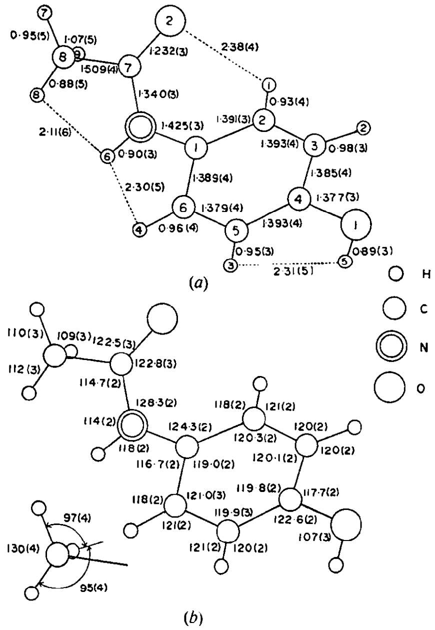

Fig. 1. The molecular structure; (*a*) bond lengths (Å) and numbering of atoms, (*b*) bond angles (°). Their e.s.d.'s are shown in parentheses.

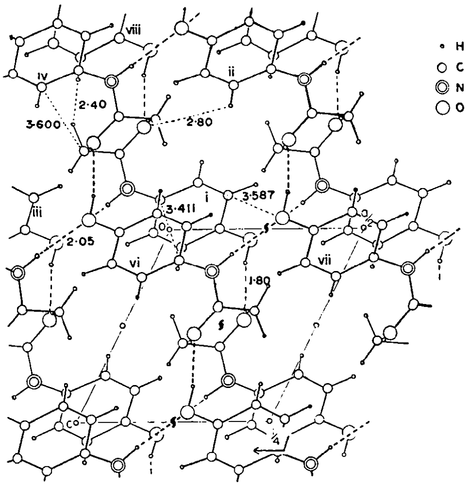

Fig. 2. The projection of the crystal structure viewed down **b**. Broken lines show hydrogen bonds, and dotted lines intermolecular contacts. Symmetry code: (i) x,y,z; (ii) $-x,1-y,-1-z$; (iii) $-\frac{1}{2}+x,\frac{1}{2}-y,z$; (iv) $-\frac{1}{2}-x,\frac{1}{2}+y,-1-z$; (v) $-x,-y,-z$; (vi) $-x,1-y,-z$; (vii) $\frac{1}{2}-x,\frac{1}{2}+y,-z$; (viii) $-\frac{1}{2}+x,\frac{1}{2}-y,-1+z$.

Table 4. *The geometry of the hydrogen bonds, in the two forms*

(*M*) and (*O*) refer to the monoclinic and orthorhombic forms respectively.

N–H···O	N···O(1)	H(6)···O(1)	N–H(6)···O(1)	N···O(1)–C(4)
(*M*) (i)···(iii)	2·934 (3) Å	2·05 (3) Å	165 (4)°	118·5 (2)°
(*O*) (i)···(iii)	2·967 (5)	2·21 (4)	159 (4)	133·7 (3)

τ[C(4),O(1),N,C(1)] = −97·2° for (*M*), −9·6° for (*O*)

O–H···O	O(1)···O(2)	H(5)···O(2)	O(1)–H(5)···O(2)	O(1)···O(2)–C(7)
(*M*) (viii)···(i)	2·663 (3)	1·80 (4)	165 (4)	140·7 (2)
(*O*) (v)···(i)	2·724 (5)	1·91 (5)	171 (5)	142·6 (3)

τ[C(4),O(1),O(2),C(7)] = −18·8° for (*M*), 23·6° for (*O*)

Symmetry codes: For the monoclinic form, as shown in Fig. 2. For the orthorhombic form, (i) x,y,z; (iii) $\frac{1}{2}+x,\frac{1}{2}-y,z$; (v) $x,\frac{1}{2}+y,\frac{1}{2}-z$.

boat conformations, the atoms C(1) and C(4) deviating from the plane of the other atoms in the ring by about +0·014 Å in the monoclinic form, and by about +0·026 Å in the orthorhombic form. The displacement of O(1) is smaller in the monoclinic than in the orthorhombic form. The dihedral angle between the benzene ring and amide group is slightly larger and the C(1)–N–C(7) angle is slightly smaller than the respective angles in the orthorhombic form. The N atom lies near the benzene ring plane, whereas that in the orthorhombic form is displaced out of the plane. Thus, the six-membered ring formed by C(1), N, C(7), O(2), H(1) and C(2) is puckered in different ways in the dimorphs, but the O(2)···H(1) distances in both forms are nearly identical.

The geometry of the hydrogen bonds is summarized in Table 4, together with that for the orthorhombic form. Notable differences are observed in their internal rotation angles, τ[C(4),O(1),N,C(1)]. The N–H···O and O–H···O hydrogen bonds link the molecules to each other to form a pleated sheet parallel to the *ac* plane. The sheets are stacked along **b** by van der Waals forces at inter-ring spacings of 3·30 and 3·35 Å. In the sheet, molecules iii and viii lie on the same side of the plane of molecule i and the dihedral angles of the benzene ring planes with respect to that of molecule i are 89·9°. On the other hand, molecules iii and v in the orthorhombic form are hydrogen bonded at dihedral angles of 27·0 and 58·4° to molecule i on both sides of its plane to form a sheet. The sheets are stacked along **c** at an inter-ring spacing of 3·41 Å. There is an overlap between the benzene ring and amide group of molecules i and vi, and *vice versa*, whereas there is no overlap in the orthorhombic form.

The following C···C contacts shorter than 3·6 Å are observed: C(1)···C(1^{vi}), C(5)···C(5^{v}) and C(8)···C(2^{iv}), and the only C···H contact shorter than 3·0 Å is C(7)···H(5^{viii}), whereas ten such contacts are observed in the orthorhombic form. The Kitaigorodsky (1973) packing coefficients amount to 0·724 and 0·750, respectively. Thus the molecular sheet of the monoclinic form is rough and thick, whereas that of the orthorhombic form is rather flat and thin, as implied by the respective lattice constants *b* and *c*. The higher melting point and lower density of the monoclinic form may be attributed to the fact that the slightly stronger hydrogen bonds cause a large dihedral angle between the molecules and hence a rather open structure.

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