

## Topochemical Studies. IX. The Crystal and Molecular Structure of *p*-Aminoacetophenone

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The crystal structure of *p*-aminoacetophenone has been determined from visually-estimated X-ray diffraction data. The crystals are monoclinic, space group  $P2_1/a$ , with cell dimensions of  $a=17.63$  (2),  $b=5.18$  (1),  $c=8.51$  (1) Å,  $\beta=106.6$  (2)° and  $Z=4$ . The final  $R$  value was 0.073 for 950 non-zero reflexions. The molecule is nearly planar, and the benzene ring takes a quinonoid form. The carbonyl O atom deviates by 0.128 Å from the plane of the benzene ring. The molecules related by a twofold screw axis are linked by a N-H...N hydrogen bond (3.217 Å) to form a chain along the  $b$  axis. The chains are held together by a N-H...O hydrogen bond (2.905 Å) between the molecules related by a  $c$ -translation to form a sheet parallel to the  $bc$  plane. The sheets are stacked by van der Waals forces at a spacing of 3.46 Å. The structure is similar to that of *p*-aminobenzamide.

### Introduction

Acetophenone is one of the most typical aromatic carbonyls which show interesting photochemical properties (Griffin, 1968; Lindqvist, 1972; Tanimoto, Hirota & Nagakura, 1975; Tanimoto, Azumi & Nagakura, 1975). From combined X-ray and neutron diffraction data, O'Connor & Maslen (1974) have concluded that the carbonyl bond in the acetyl group attached to the benzene ring is strongly polar. It is of additional interest that aminoacetophenone derivatives possess some degree of local anaesthetic activity (Boido & Di Maio-Cappello, 1974).

As part of the topochemical studies (part VIII: Haisa, Kashino, Ikejiri, Ohno & Teranishi, 1976), the structure determination of *p*-aminoacetophenone was undertaken to investigate the effect of the occurrence of an amino group, which has both electron-donating properties and the ability to form hydrogen bonds, on the molecular structure and molecular overlapping in the crystals.

### Experimental

The crystals were obtained from an ethanol solution as prisms elongated along the  $b$  axis. Density was measured by flotation in a mixture of carbon tetrachloride and xylene. The crystal data are: *p*-aminoacetophenone  $C_8H_9NO$ , M.W. 135.2, m.p. 110°C. Monoclinic, space group  $P2_1/a$ ,  $a=17.63$  (2),  $b=5.18$  (1),  $c=8.51$  (1) Å,  $\beta=106.6$  (2)°,  $U=744.7$  Å<sup>3</sup>,  $D_m=1.20$ ,  $D_x=1.21$  g cm<sup>-3</sup> for  $Z=4$ ,  $F(000)=288$ ,  $\mu=6.6$  cm<sup>-1</sup> for Cu  $K\alpha$  ( $\lambda=1.5418$  Å).

Intensity data were collected on equi-inclination Weissenberg photographs for the layers  $hk0$  to  $hk6$  and  $h0l$  to  $h4l$  with specimens of dimensions 0.27 × 0.31 × 0.41 and 0.30 × 0.40 × 0.15 mm, respectively. Lorentz and polarization, and shape corrections were applied and intensities of the 950 independent reflexions were placed on an approximately absolute scale by a Wilson plot ( $B=5.8$  Å<sup>2</sup>).

### Structure determination and refinement

The structure was solved by the Patterson method and refined by block-diagonal least-squares calculations. At the stage of an  $R$  value of 0.11 all the H atoms were located by a difference Fourier synthesis. With anisotropic thermal parameters for the non-hydrogen atoms and the weighting scheme:  $w=1.0$  for  $0 < |F_o| \leq 4.0$  and  $w=(4.0/|F_o|)^2$  for  $|F_o| > 4.0$ , the refinement reduced the  $R$  value to 0.073.\*

The final atomic parameters are listed in Table 1. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The

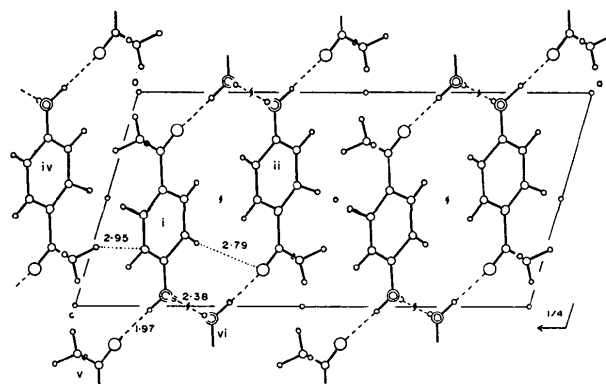


Fig. 1. Projection of the crystal structure viewed down the  $b$  axis. Broken lines show hydrogen bonds, and dotted lines intermolecular contacts.

Symmetry code: i  $x, y, z$ ; ii  $\frac{1}{2} - x, -\frac{1}{2} + y, 1 - z$ ; iii  $x, -1 + y, z$ ; iv  $-x, 1 - y, 1 - z$ ; v  $x, y, 1 + z$ ; vi  $\frac{1}{2} - x, -\frac{1}{2} + y, 2 - z$ ; vii  $\frac{1}{2} - x, \frac{1}{2} + y, 2 - z$ .

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31367 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic parameters

Positional and thermal parameters for the non-hydrogen atoms ( $\times 10^4$ ) with their e.s.d.'s in parentheses. The  $\beta_{ij}$ 's are defined by:  
 $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - hk\beta_{12} - hl\beta_{13} - kl\beta_{23})$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
O	1113 (2)	5127 (6)	1763 (3)	83 (1)	1041 (19)	196 (4)	-73 (8)	81 (4)	22 (14)
N	1946 (2)	6820 (6)	9453 (3)	61 (1)	659 (14)	186 (5)	-29 (7)	37 (4)	-36 (13)
C(1)	1176 (2)	4549 (6)	4519 (4)	38 (1)	491 (13)	192 (5)	35 (6)	45 (4)	17 (12)
C(2)	1705 (2)	6579 (6)	5034 (4)	47 (1)	507 (13)	203 (5)	-8 (6)	67 (4)	55 (14)
C(3)	1966 (2)	7322 (6)	6644 (4)	42 (1)	509 (13)	223 (5)	-22 (6)	43 (4)	2 (14)
C(4)	1687 (2)	6091 (6)	7832 (4)	45 (1)	480 (13)	180 (5)	24 (6)	40 (4)	49 (13)
C(5)	1163 (2)	4024 (7)	7339 (4)	57 (1)	548 (15)	199 (6)	-60 (7)	62 (5)	68 (14)
C(6)	916 (2)	3304 (6)	5726 (4)	51 (1)	513 (14)	211 (6)	-41 (7)	47 (4)	-9 (14)
C(7)	905 (2)	3870 (7)	2773 (4)	54 (1)	604 (16)	193 (6)	68 (7)	43 (4)	-9 (15)
C(8)	361 (3)	1621 (8)	2214 (5)	79 (2)	696 (19)	246 (7)	-28 (10)	2 (6)	-208 (19)

Table 1 (cont.)

Positional ( $\times 10^3$ ) and isotropic thermal parameters for the hydrogen atoms.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
H(1)	211 (2)	848 (7)	958 (4)	4.8 (0.8)
H(2)	166 (2)	630 (7)	1017 (5)	6.2 (1.0)
H(3)	187 (2)	757 (8)	419 (5)	6.3 (1.0)
H(4)	228 (2)	892 (6)	697 (4)	3.5 (0.7)
H(5)	94 (2)	324 (8)	815 (5)	5.5 (0.9)
H(6)	42 (2)	198 (7)	534 (5)	5.2 (0.9)
H(7)	53 (3)	6 (10)	235 (7)	8.9 (1.3)
H(8)	11 (3)	195 (12)	114 (7)	10.7 (1.5)
H(9)	-8 (3)	161 (11)	272 (6)	9.7 (1.4)

computation was carried out on an NEAC 2200-500 computer at the Okayama University Computer Centre. The programs used were *HBL5-5* and *DAPH* (Ashida, 1973).

### Results and discussion

Projection of the crystal structure viewed down the *b* axis is illustrated in Fig. 1. Bond lengths and angles

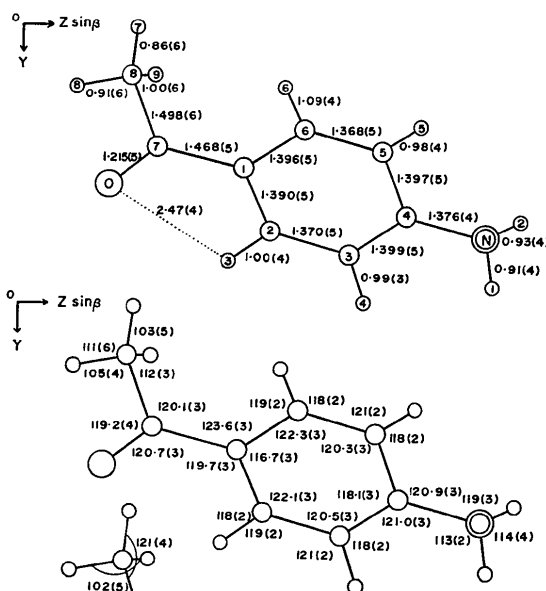


Fig. 2. Bond lengths (Å) and angles (°) with their e.s.d.'s in parentheses.

are shown in Fig. 2. The displacements of the atoms from the least-squares planes of the benzene ring and the acetyl group are listed in Table 2. The molecule is essentially planar with the dihedral angle between the acetyl group and the benzene ring of 4.0°, which is comparable to 3.4° in acetophenone (Tanimoto, Kobayashi, Nagakura & Saito, 1973).

Table 2. The least-squares planes and deviations from the planes

$$X = ax + cz \cos \beta, Y = by, Z = cz \sin \beta$$

(I) Benzene ring:  $0.7510X - 0.6411Y + 0.1580Z + 0.1957 = 0$

Atom	Shift (Å)	Atom	Shift (Å)	Atom	Shift (Å)
C(1)*	-0.001	C(7)	-0.040	H(1)	-0.34
C(2)*	-0.003	C(8)	0.016	H(2)	-0.24
C(3)*	0.010	O	-0.128	H(3)	-0.06
C(4)*	-0.015	N	-0.000	H(4)	-0.11
C(5)*	0.006			H(5)	-0.08
C(6)*	0.004			H(6)	-0.19

(II) Acetyl group:  $0.7905X - 0.6013Y + 0.1165Z + 0.2165 = 0$

Atom	Shift (Å)	Atom	Shift (Å)	Atom	Shift (Å)
C(1)*	-0.001	O*	-0.001	H(7)	0.71
C(7)*	0.003	C(2)	0.054	H(8)	-0.35
C(8)*	-0.001	C(6)	-0.092	H(9)	-0.67

\* Atoms used for the calculation of the planes.

The bond lengths, C(1)-C(7), C(2)-C(3) and C(5)-C(6), are shorter than those in acetophenone and *p*-hydroxyacetophenone (Vainshtein, Lobanova & Gurskaya, 1974). The angles, C(2)-C(1)-C(6) and C(3)-C(4)-C(5), are smaller than the  $sp^2$  angle which indicates through-conjugation (Domenicano, Vaciago & Coulson, 1975). The shortening of bond lengths and the narrowing of bond angles suggest that the molecule takes a quinonoid form because of interaction between a strong  $\pi$ -donor and a  $\pi$ -acceptor. Such a quinonoid structure has been found in *p*-aminobenzoic acid (Lai & Marsh, 1967), 2-(*p*-dimethylanilino)-4-phenyl-6-thiathiophthene (Hordvik & Saethre, 1972), *N,N,N',N'*-tetramethylphenylenediamine radical cation (de Boer & Vos, 1972) and *N,N*-dimethyl-*p*-nitrosoaniline (Rømming & Talberg, 1973). Kim, Boyko & Carpenter (1973) have shown that *p*-nitroacetophenone takes a quinonoid form and ascribed it to

the substitution of two electron-withdrawing groups. A further example has also been reported for terephthalic acid (Bailey & Brown, 1967).

The molecules related by a twofold screw axis at  $x = \frac{1}{4}$  and  $z = 0$  are linked by N-H...N hydrogen bonds between the amino groups to form a chain along the  $b$  axis. The chains are held together side by side through the N-H...O hydrogen bond between the amino group and the carbonyl group of the molecule related by a  $c$ -translation to form a sheet parallel to the  $bc$  plane. The sheet consists of the molecules related by a twofold screw axis at  $x = \frac{1}{4}$  and  $z = \frac{1}{2}$ . The benzene rings make an angle of  $79.7^\circ$  to each other. The sheets are stacked by van der Waals forces at a spacing of  $3.46 \text{ \AA}$ , their molecular overlapping and stacking mode being illustrated in Fig. 3.

It is of particular interest to compare the structure with that of *p*-aminobenzamide (Alléaume & Decap, 1965). Their cell dimensions and structural features are similar to each other as seen from Table 3. But in the present compound the N...O<sup>v</sup>-C(7<sup>v</sup>) angle is close to the digonal angle rather than the  $sp^2$  angle. The amide group in *p*-aminobenzamide is largely twisted about the C(1)-C(7) bond by the additional hydrogen bonds.

Table 3. The correspondence of structural features of *p*-aminoacetophenone with those of *p*-aminobenzamide

	$\text{H}_2\text{NC}_6\text{H}_4\text{COCH}_3$	$\text{H}_2\text{NC}_6\text{H}_4\text{CONH}_2$
Cell constants	$a = 17.63 \text{ \AA}$ $b = 5.18$ $c = 8.51$ $\beta = 106.6^\circ$	$c = 7.91 \text{ \AA}$ $b = 5.29$ $a = 8.42$ $\beta = 108.0^\circ$
Space group	$P2_1/a$	$P2_1$
Dihedral angle between the benzene ring planes related by the twofold screw axis	$79.7^\circ$	$71.2^\circ$
Geometry of hydrogen bonds		
N...O <sup>v</sup>	$2.905 (4) \text{ \AA}$	$2.97 \text{ \AA}$
N...H(2)...O <sup>v</sup>	$177 (4)^\circ$	—
N...O <sup>v</sup> —C(7 <sup>v</sup> )	$162.4 (3)$	$117.7$
N...N <sup>vii</sup>	$3.217 (6) \text{ \AA}$	$3.18 \text{ \AA}$
N—H(1)...N <sup>vii</sup>	$154 (3)^\circ$	—
C(4)—N...O <sup>v</sup>	$120.5 (2)$	$122.2$
C(4)—N...N <sup>vii</sup>	$120.8 (2)$	$116.2$
C(4)—N...N <sup>vi</sup>	$94.0 (2)$	$95.4$
O <sup>v</sup> ...N...N <sup>vii</sup>	$115.5 (1)$	$107.0$
O <sup>v</sup> ...N...N <sup>vi</sup>	$86.8 (1)$	$101.7$
N <sup>vii</sup> ...N...N <sup>vi</sup>	$107.2 (1)$	$112.5$
N <sub>(amide)</sub> —H...O	none	$2.95, 3.13 \text{ \AA}$
Dihedral angle between the benzene ring and acetyl (or amide) group	$4.0^\circ$	$27.2^\circ$

Symmetry code is given in Fig. 1.

### References

- ALLÉAUME, M. & DECAP, J. (1965). *C. R. Acad. Sci. Paris*, **260**, 5790–5792.  
 ASHIDA, T. (1973). *The Universal Crystallographic Computing System—Osaka*, The Computation Centre, Osaka Univ.  
 BAILEY, M. & BROWN, C. J. (1967). *Acta Cryst.* **22**, 387–391.  
 BOER, J. J. DE & VOS, A. (1972). *Acta Cryst.* **B28**, 839–848.

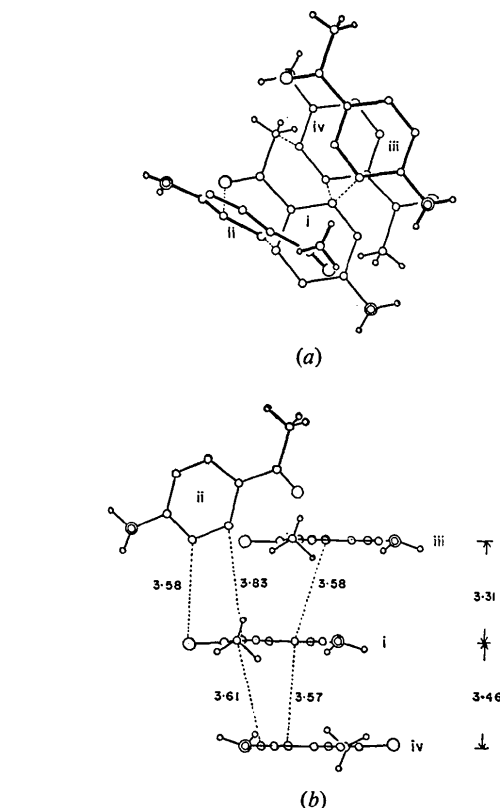


Fig. 3. The molecular overlapping (a) and stacking (b) with inter-ring spacings (Å), along with some intermolecular distances (Å). Hydrogen atoms of the benzene ring are omitted. Symmetry code is given in Fig. 1.

- BOIDO, V. & DI MAIO-CAPELLO, B. (1974). *Boll. Chim. Farm.* **113**, 344–349.  
 DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* **B31**, 221–234.  
 GRIFFIN, R. N. (1968). *Photochem. Photobiol.* **7**, 159–173.  
 HAISA, M., KASHINO, S., IKEJIRI, F., OHNO, T. & TERANISHI, K. (1976). *Acta Cryst.* **B32**, 857–860.  
 HORDVIK, A. & SÆTHRE, L. J. (1972). *Acta Chem. Scand.* **26**, 3114–3130.  
*International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.  
 KIM, J. K. S., BOYKO, E. R. & CARPENTER, G. B. (1973). *Acta Cryst.* **B29**, 1141–1144.  
 LAI, T. F. & MARSH, R. E. (1967). *Acta Cryst.* **22**, 885–893.  
 LINDQVIST, L. (1972). *J. Phys. Chem.* **76**, 821–822.  
 O'CONNOR, B. H. & MASLEN, E. N. (1974). *Acta Cryst.* **B30**, 383–389.  
 RØMMING, C. & TALBERG, H. J. (1973). *Acta Chem. Scand.* **27**, 2246–2248.  
 TANIMOTO, Y., AZUMI, T. & NAGAKURA, S. (1975). *Bull. Chem. Soc. Japan*, **48**, 136–139.  
 TANIMOTO, Y., HIROTA, N. & NAGAKURA, S. (1975). *Bull. Chem. Soc. Japan*, **48**, 41–45.  
 TANIMOTO, Y., KOBAYASHI, H., NAGAKURA, S. & SAITO, Y. (1973). *Acta Cryst.* **B29**, 1822–1826.  
 VAINSHTEIN, B. K., LOBANOVA, G. M. & GURSKAYA, G. V. (1974). *Kristallografiya*, **19**, 531–538.