

The Structures of *N*-Aromatic Amides: *p*-Acetanisidide, *N*-2-Naphthylacetamide and *N*-2-Fluorenylacetamide

BY MASAO HAISA, SETSUO KASHINO, TETSUO UENO, NOBUHISA SHINOZAKI AND YOSUKE MATSUZAKI

Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700, Japan

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Abstract

The crystal structures of the *N*-aromatic amides *p*-acetanisidide [*N*-(4-methoxyphenyl)acetamide] (AAS), *N*-2-naphthylacetamide (NAA) and *N*-2-fluorenylacetamide (FAA) have been determined from visually estimated Cu *K* α data, and refined to *R* values of 0.076, 0.075 and 0.061 for 1233, 1427 and 1023 non-zero reflexions respectively. The crystal data are: *Pcab*, *a* = 9.32 (1), *b* = 25.13 (2), *c* = 7.691 (5) Å, *Z* = 8 for AAS; *Pcab*, *a* = 9.651 (6), *b* = 28.23 (3), *c* = 7.518 (8) Å, *Z* = 8 for NAA; and *Cc*, *a* = 16.77 (3), *b* = 4.830 (6), *c* = 15.85 (2) Å, β = 115.4 (1)°, *Z* = 4 for FAA. The structures of AAS and NAA are homomorphous with that of acetanilide. The molecules related by a 2₁ axis parallel to *a* are linked together by an N–H···O hydrogen bond to form a ribbon. The ribbons are held together by interactions between the aromatic rings related by a *c* glide. The dihedral angles between the rings are 75.3° for AAS and 54.0° for NAA, being close to those in benzene and naphthalene respectively. In FAA, the molecules related by a *b* translation are linked together by an N–H···O hydrogen bond to form a ribbon. The ribbon is stabilized by the parallel stacking of the aromatic rings. The morphotropism in the crystal structures of the *N*-aromatic amides is discussed in relation to the respective types of hydrogen bond.

Introduction

The present work on *N*-aromatic amides forms part of a systematization of the crystal structures of aromatic compounds (Haisa, 1978). As an extension of the study of the dimorphs of 4-methylacetanilide (Haisa, Kashino, Matsuzaki, Kawai & Kunitomi, 1977), the morphotropic relationship of the crystal structures of the title compounds has been examined.

Experimental

The crystals of AAS, NAA and FAA were grown by slow evaporation from ethanol solutions as colourless

single crystals. Intensities were estimated visually on equi-inclination Weissenberg photographs and were corrected for Lorentz and polarization factors, and for spot shape. The data were put on an approximately absolute scale by Wilson's plot. Crystal data and experimental details are summarized in Table 1. The systematic absences for FAA showed the possible space groups to be *Cc* and *C2/c*, but the latter was ruled out by the structure analysis.

Structure determination and refinement

All the structures were solved by the Patterson method. The H atoms were located from the difference maps. The refinements were made by block-diagonal least-squares calculations. The weighting scheme at the later

Table 1. Crystal data and experimental details

	<i>p</i> -Acetanisidide (AAS)	<i>N</i> -2-Naphthylacetamide (NAA)	<i>N</i> -2-Fluorenylacetamide (FAA)
<i>M_r</i>	C ₉ H ₁₁ NO ₂	C ₁₇ H ₁₃ NO	C ₁₇ H ₁₃ NO
M.p. (K)	165.2	185.2	223.3
Crystal system	403.5–404.5	406–408	472–473
Morphology	Orthorhombic	Orthorhombic	Monoclinic
	Plates developed (010)	Plates developed (010)	Hexagonal prisms elongated along <i>b</i> bounded by {100}, {001} and {101}
Systematic absences	<i>Ok</i> l, <i>l</i> odd <i>h</i> 0l, <i>h</i> odd <i>hk</i> 0, <i>k</i> odd	<i>Ok</i> l, <i>l</i> odd <i>h</i> 0l, <i>h</i> odd <i>hk</i> 0, <i>k</i> odd	<i>hkl</i> , <i>h</i> + <i>k</i> odd <i>h</i> 0l, <i>l</i> odd
Space group	<i>Pcab</i> (<i>D</i> _{2h} ¹⁶)	<i>Pcab</i> (<i>D</i> _{2h} ¹⁶)	<i>Cc</i> (<i>C</i> _{2h} ²)
<i>a</i> (Å)	9.32 (1)	9.651 (6)	16.77 (3)
<i>b</i> (Å)	25.13 (2)	28.23 (3)	4.830 (6)
<i>c</i> (Å)	7.691 (5)	7.518 (8)	15.85 (2)
β (°)			115.4 (1)
<i>V</i> (Å ³)	1802 (3)	2046 (3)	1159 (2)
<i>Z</i>	8	8	4
<i>D_x</i> (Mg m ⁻³)	1.218	1.202	1.279
<i>D_m</i> (Mg m ⁻³)	1.24	1.20	1.27
Flotation mixture	KI–H ₂ O	KBr–H ₂ O	KI–H ₂ O
μ (mm ⁻¹) for Cu <i>K</i> α	0.70	0.62	0.64
<i>F</i> (000)	704	784	472
Dimensions of specimens used (mm)	0.17 × 0.10 × 0.27 0.50 × 0.15 × 0.17	0.30 × 0.30 × 1.0 0.90 × 0.17 × 0.22	0.30 × 0.80 × 0.20 0.50 × 0.30 × 0.20
Layers photographed	<i>hk</i> 0 to <i>hk</i> 6 <i>Ok</i> l to <i>7kl</i>	<i>hk</i> 0 to <i>hk</i> 5 <i>Ok</i> l to <i>7kl</i>	<i>h</i> 0l to <i>h</i> 4l <i>Ok</i> l to <i>2kl</i>
Non-zero reflexions	1233	1427	1023
Percentage accessible	60.1	61.0	77.1
<i>B</i> (Å ²) from Wilson's plot	5.0	4.8	4.8

Table 2. The final atomic parameters of the non-hydrogen atoms ($\times 10^4$, except B_{eq}) and of the hydrogen atoms ($\times 10^3$, except B_{iso}) with e.s.d.'s in parentheses

	x	y	z	B_{eq} or B_{iso} (\AA^2)
<i>p</i> -Acetanisidide (AAS)				
O(1)	2428 (3)	5082 (1)	3523 (4)	5.1 (1)
O(2)	3592 (3)	2565 (1)	4718 (3)	5.6 (1)
N	4606 (3)	4705 (1)	2923 (3)	3.8 (1)
C(1)	4342 (3)	4167 (1)	3449 (4)	3.5 (1)
C(2)	3246 (3)	4018 (1)	4595 (4)	3.9 (1)
C(3)	3043 (4)	3480 (1)	4991 (4)	4.3 (1)
C(4)	3925 (4)	3088 (1)	4276 (4)	4.1 (1)
C(5)	5063 (4)	3235 (1)	3188 (4)	4.2 (1)
C(6)	5263 (3)	3774 (1)	2787 (4)	3.9 (1)
C(7)	3648 (3)	5116 (1)	2934 (4)	3.7 (1)
C(8)	4201 (4)	5637 (1)	2123 (5)	4.8 (2)
C(9)	4216 (6)	2151 (2)	3665 (6)	6.6 (2)
H(1)	254 (4)	427 (1)	508 (5)	3.0 (8)
H(2)	219 (5)	341 (2)	566 (6)	3.9 (9)
H(3)	579 (4)	294 (2)	262 (5)	3.9 (9)
H(4)	602 (4)	386 (1)	192 (5)	2.4 (7)
H(5)	554 (4)	478 (1)	267 (5)	2.7 (8)
H(6)	516 (4)	568 (2)	202 (6)	5.9 (12)
H(7)	357 (5)	568 (2)	108 (6)	5.5 (12)
H(8)	397 (5)	591 (2)	306 (5)	4.3 (10)
H(9)	388 (4)	220 (2)	229 (5)	3.6 (9)
H(10)	368 (6)	182 (2)	410 (7)	6.5 (13)
H(11)	528 (5)	211 (2)	383 (6)	5.5 (11)
<i>N</i> -2-Naphthylacetamide (NAA)				
O	-986 (2)	30 (1)	2902 (3)	5.4 (1)
N	1159 (2)	245 (1)	1977 (3)	4.2 (1)
C(1)	-254 (2)	969 (1)	1713 (3)	4.2 (1)
C(2)	909 (2)	706 (1)	1323 (3)	4.0 (1)
C(3)	1953 (2)	895 (1)	217 (4)	4.7 (1)
C(4)	1815 (3)	1333 (1)	-508 (4)	5.2 (1)
C(5)	410 (3)	2060 (1)	-959 (4)	6.1 (1)
C(6)	-761 (4)	2312 (1)	-603 (5)	6.9 (2)
C(7)	-1773 (3)	2132 (1)	536 (4)	6.3 (2)
C(8)	-1626 (3)	1697 (1)	1304 (4)	5.5 (1)
C(9)	-426 (2)	1423 (1)	958 (3)	4.4 (1)
C(10)	615 (3)	1609 (1)	-176 (3)	4.7 (1)
C(11)	236 (2)	-66 (1)	2651 (3)	4.2 (1)
C(12)	822 (3)	-545 (1)	3088 (4)	5.1 (1)
H(1)	-101 (3)	83 (1)	256 (4)	4.0 (6)
H(2)	275 (3)	69 (1)	-6 (4)	3.3 (6)
H(3)	256 (3)	145 (1)	-131 (4)	4.7 (7)
H(4)	120 (3)	218 (1)	-185 (4)	5.0 (8)
H(5)	-97 (4)	261 (1)	-121 (5)	7.5 (10)
H(6)	-256 (3)	232 (1)	78 (4)	5.5 (8)
H(7)	-242 (3)	156 (1)	213 (4)	4.4 (7)
H(8)	206 (3)	15 (1)	185 (4)	3.8 (6)
H(9)	166 (4)	-53 (1)	385 (5)	6.1 (9)
H(10)	121 (6)	-66 (2)	204 (6)	10.7 (14)
H(11)	21 (4)	-77 (2)	362 (6)	10.4 (15)
<i>N</i> -2-Fluorenylacetamide (FAA)				
O	1438 (2)	3766 (6)	3497 (3)	5.2 (2)
N	1941 (2)	-477 (7)	3323 (3)	3.8 (1)
C(1)	2211 (3)	2423 (8)	2195 (3)	3.6 (2)
C(2)	2493 (3)	392 (8)	2898 (3)	3.5 (2)
C(3)	3313 (3)	-818 (10)	3197 (3)	4.0 (2)
C(4)	3866 (3)	-81 (10)	2788 (3)	4.1 (2)
C(5)	4842 (3)	2540 (12)	1561 (4)	4.8 (2)
C(6)	5091 (3)	3971 (12)	944 (4)	5.4 (2)

Table 2 (cont.)

	x	y	z	B_{eq} or B_{iso} (\AA^2)
C(7)	4533 (4)	5920 (12)	328 (4)	5.6 (2)
C(8)	3726 (3)	6500 (11)	309 (3)	4.8 (2)
C(9)	2620 (3)	5258 (9)	1031 (3)	3.7 (2)
C(10)	2765 (3)	3134 (9)	1791 (3)	3.4 (2)
C(11)	3599 (2)	1913 (9)	2088 (3)	3.5 (2)
C(12)	4033 (3)	3104 (9)	1533 (3)	3.7 (2)
C(13)	3468 (3)	5062 (9)	906 (3)	3.8 (2)
C(14)	1462 (3)	1228 (8)	3594 (3)	3.6 (1)
C(15)	938 (4)	-130 (10)	4043 (4)	5.2 (2)
H(1)	170 (4)	338 (12)	203 (4)	2.3 (10)
H(2)	336 (5)	-224 (17)	364 (6)	5.5 (18)
H(3)	446 (4)	-105 (11)	298 (4)	2.6 (10)
H(4)	523 (4)	115 (12)	212 (4)	2.6 (10)
H(5)	555 (5)	374 (13)	80 (5)	4.4 (14)
H(6)	470 (6)	722 (16)	-7 (6)	4.9 (16)
H(7)	335 (6)	791 (16)	-11 (6)	5.2 (16)
H(8)	213 (4)	463 (12)	42 (4)	2.7 (11)
H(9)	251 (3)	721 (10)	117 (4)	1.7 (9)
H(10)	184 (3)	-242 (9)	335 (3)	1.4 (9)
H(11)	26 (6)	16 (18)	356 (6)	6.3 (19)
H(12)	90 (7)	81 (17)	459 (7)	7.5 (22)
H(13)	101 (5)	-195 (16)	403 (6)	5.3 (17)

stages was: $w = 1.0$ for $0 < |F_o| \leq F_{max}$, $w = (F_{max}/|F_o|)^2$ for $|F_o| > F_{max}$, F_{max} being 10.0 for AAS, and 6.0 for both NAA and FAA. The correction for extinction effects was applied for AAS at the stage $R = 0.088$, according to $I_{corr} = I_{obs}/(1 - gI_{obs})$ with $g = 2.75 \times 10^{-5}$ for the eleven strongest reflexions (022, 201, 202, 211, 122, 121, 200, 040, 112, 120 and 111). The final R values for the non-zero reflexions were 0.076 for AAS, 0.075 for NAA, and 0.061 for FAA. The final atomic parameters are listed in Table 2.*

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The computations were carried out at the Okayama University Computer Center. The programs used were *SIGM*, *HBL5-5* and *DAPH* (Ashida, 1973).

Description and discussion of the structures

Molecular structures

Bond lengths and angles are shown in Fig. 1. The displacements of the atoms from the least-squares planes are listed in Table 3.

In AAS, all the non-hydrogen atoms of the methoxy and amido groups deviate to the same side of the plane of the benzene ring, which takes a boat conformation. C(4)-O(2) is slightly longer than in anisic acid (Colapietro & Domenicano, 1978) and the other

* Lists of structure factors and anisotropic thermal parameters for AAS, NAA and FAA have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35344 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

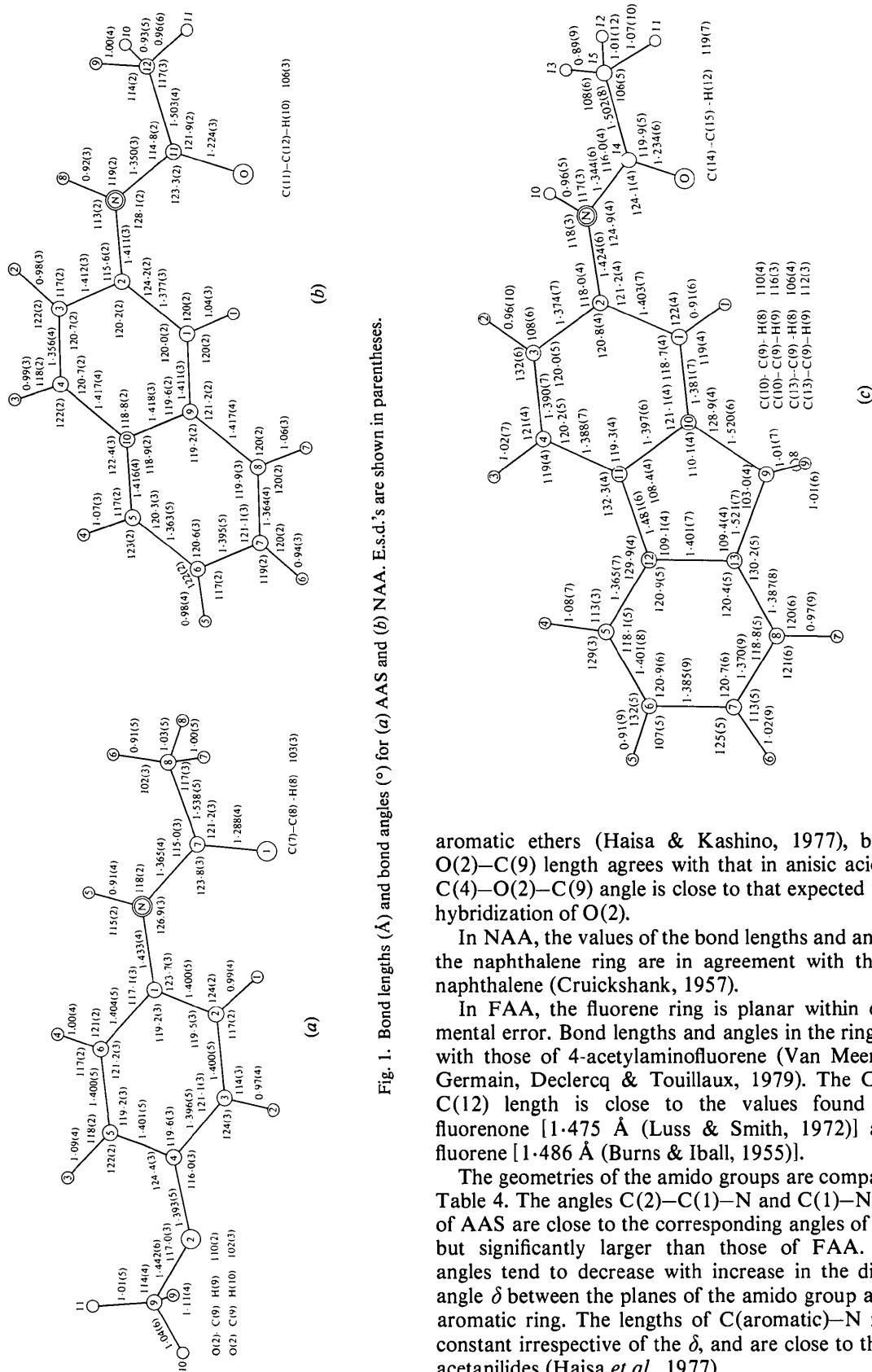


Fig. 1. Bond lengths (Å) and bond angles (°) for (a) AAS and (b) NAA. E.s.d.'s are shown in parentheses.

aromatic ethers (Haisa & Kashino, 1977), but the O(2)–C(9) length agrees with that in anisic acid. The C(4)–O(2)–C(9) angle is close to that expected for sp^2 hybridization of O(2).

In NAA, the values of the bond lengths and angles in the naphthalene ring are in agreement with those in naphthalene (Cruickshank, 1957).

In FAA, the fluorene ring is planar within experimental error. Bond lengths and angles in the ring agree with those of 4-acetylaminofluorene (Van Meerse, Germain, Declercq & Touillaux, 1979). The C(11)–C(12) length is close to the values found in 9-fluorenone [1.475 Å (Luss & Smith, 1972)] and in fluorene [1.486 Å (Burns & Iball, 1955)].

The geometries of the amido groups are compared in Table 4. The angles C(2)–C(1)–N and C(1)–N–C(7) of AAS are close to the corresponding angles of NAA, but significantly larger than those of FAA. These angles tend to decrease with increase in the dihedral angle δ between the planes of the amido group and the aromatic ring. The lengths of C(aromatic)–N remain constant irrespective of the δ , and are close to those in acetanilides (Haisa *et al.*, 1977).

Table 3. The least-squares planes and displacements (Å) of atoms from the planes

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

(a) *p*-Acetanisidide (AAS)

Benzene ring

$$-0.611X - 0.096Y - 0.786Z + 5.581 = 0$$

C(1)*	0.020 (3)	C(2)*	-0.012 (3)	C(3)*	-0.006 (4)
C(4)*	0.017 (4)	C(5)*	-0.009 (4)	C(6)*	-0.010 (3)
O(2)	0.066 (3)	N	0.058 (3)	C(7)	0.498 (3)
O(1)	0.846 (3)	C(8)	0.548 (4)	C(9)	0.446 (5)

Amido group

$$-0.399X - 0.290Y - 0.8957Z + 6.896 = 0$$

O(1)*	0.001 (3)	N*	0.001 (3)	C(7)*	-0.003 (3)
C(8)*	0.001 (4)	C(1)	0.114 (3)		

(b) *N*-2-Naphthylacetamide (NAA)

Naphthalene ring

$$-0.454X - 0.415Y - 0.788Z + 2.036 = 0$$

C(1)*	-0.002 (2)	C(2)*	0.028 (2)	C(3)*	0.002 (3)
C(4)*	-0.020 (3)	C(5)*	0.011 (3)	C(6)*	0.018 (4)
C(7)*	-0.001 (3)	C(8)*	-0.011 (3)	C(9)*	-0.011 (2)
C(10)*	-0.014 (3)	N	0.070 (2)	C(11)	0.440 (2)
O	0.714 (2)	C(12)	0.486 (3)		

Amido group

$$-0.219X - 0.314Y - 0.924Z + 1.833 = 0$$

O*	-0.001 (2)	N*	-0.001 (2)	C(11)*	0.002 (2)
C(12)*	-0.001 (3)	C(2)	0.098 (2)		

(c) *N*-2-Fluorenylacamide (FAA)

Fluorene ring

$$-0.121X - 0.713Y - 0.690Z + 3.266 = 0$$

C(1)*	0.004 (5)	C(2)*	0.013 (5)	C(3)*	-0.007 (5)
C(4)*	-0.005 (5)	C(5)*	-0.001 (6)	C(6)*	0.011 (6)
C(7)*	0.008 (7)	C(8)*	-0.010 (6)	C(9)*	-0.008 (5)
C(10)*	0.010 (4)	C(11)*	-0.007 (4)	C(12)*	-0.006 (5)
C(13)*	-0.000 (5)	N	0.041 (4)	C(14)	-0.693 (4)
O	-1.475 (4)	C(15)	-0.523 (6)		

Amido group

$$-0.431X - 0.094Y - 0.898Z + 4.649 = 0$$

O*	-0.001 (4)	N*	-0.000 (4)	C(14)*	0.001 (4)
C(15)*	-0.000 (6)	C(2)	-0.020 (5)		

* Atoms used for the calculation of the planes.

Table 4. Geometries of the amido groups

Bond lengths are in Å, angles in degrees. The numbering of the atoms corresponds to that of AAS.

	NAA	AAS	FAA
δ^*	16.7 (4)	20.3 (5)	42.4 (7)
C(2)-C(1)-N	124.2 (2)	123.7 (3)	121.2 (4)
C(1)-N-C(7)	128.1 (2)	126.9 (3)	124.9 (4)
N-C(7)-O	123.3 (2)	123.8 (3)	124.1 (4)
N-C(7)-C(8)	114.8 (2)	115.0 (3)	116.0 (4)
C(1)-N	1.411 (3)	1.433 (4)	1.424 (6)
C(7)-N	1.350 (3)	1.365 (4)	1.344 (6)
C(7)-O	1.224 (3)	1.228 (4)	1.234 (6)

 δ^* is the dihedral angle ($^\circ$) between the planes of the amido group and the aromatic ring.

Crystal structures

Projections of the crystal structures are shown in Fig. 2. The structures of AAS and NAA are homomorphous (Haisa, 1978) with that of acetanilide (Brown, 1966). In these crystals, the molecules related by a 2_1 axis parallel to a are linked together by an N-H...O hydrogen bond [N...O 2.905 (4), H...O 2.02 (4) Å, N-H...O 165 (3) $^\circ$ for AAS; N...O

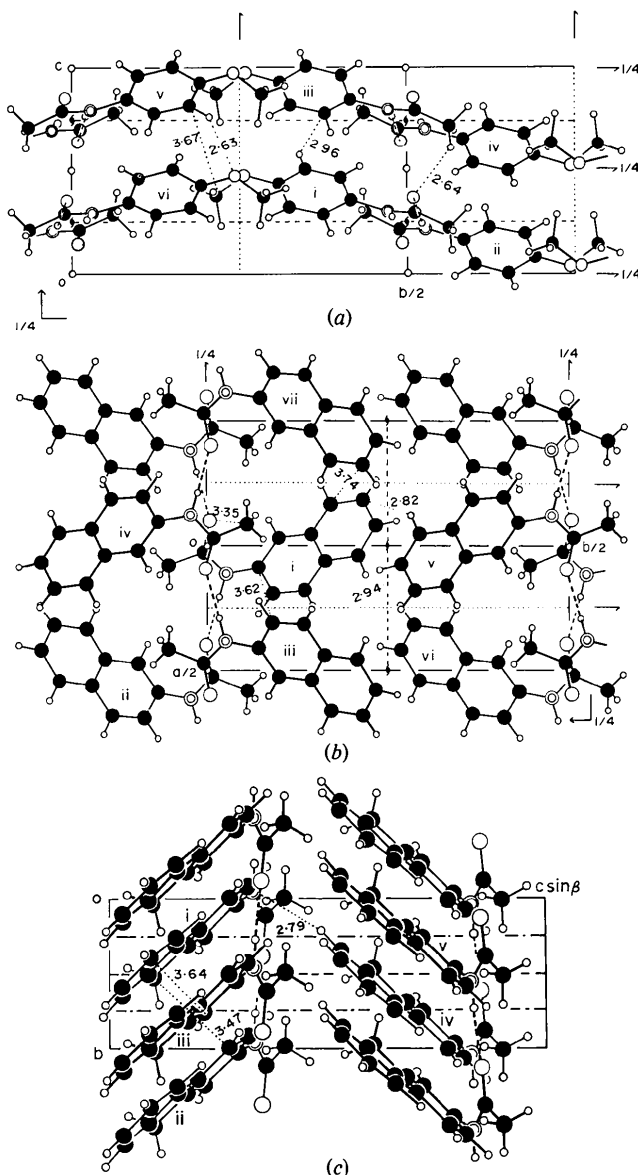


Fig. 2. Projections of the crystal structures. (a) AAS viewed along a , (b) NAA viewed along c , and (c) FAA viewed along a . Broken lines show hydrogen bonds, and dotted lines intermolecular contacts. Symmetry code: for AAS: (i) x, y, z ; (ii) $-\frac{1}{2} + x, 1 - y, \frac{1}{2} - z$; (iii) $\frac{1}{2} - x, y, \frac{1}{2} + z$; (iv) $-x, 1 - y, 1 - z$; (v) $1 - x, \frac{1}{2} - y, \frac{1}{2} + z$; (vi) $\frac{1}{2} + x, \frac{1}{2} - y, z$; for NAA: (i) x, y, z ; (ii) $\frac{1}{2} + x, -y, \frac{1}{2} - z$; (iii) $\frac{1}{2} - x, y, \frac{1}{2} + z$; (iv) $-x, -y, 1 - z$; (v) $-x, \frac{1}{2} - y, \frac{1}{2} + z$; (vi) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (vii) $-\frac{1}{2} - x, y, \frac{1}{2} + z$; for FAA: (i) x, y, z ; (ii) $x, 1 + y, z$; (iii) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (iv) $x, -y, \frac{1}{2} + z$; (v) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

Table 5. Characteristic features of the crystal structure and the N—H...O=C hydrogen bond of aromatic amides, ArNHCOR

Compound	Ar	R	Space group	Z	<i>D</i> * (Å)	θ^\dagger (°)	δ^\ddagger (°)	N...O (Å)	H...O (Å)	\angle N—H...O (°)	\angle C=O...N (°)
(1) 2_1 type											
(a)	C ₆ H ₅	Me	<i>Pbca</i>	8	9.483	17.6	17.4	2.943	1.86	180	139.1
(b)	MeOC ₆ H ₄	Me	<i>Pcab</i>	8	9.32	19.8	20.3	2.905	2.02	165	133.3
(c)	C ₁₀ H ₇	Me	<i>Pcab</i>	8	9.651	12.6	16.7	2.865	1.96	168	150.5
(d)	MeC ₆ H ₄	Me	<i>P2₁/c</i>	4	9.59	14.9	18.7	2.923	2.05	178	141.9
(e)	ClCF ₃ C ₆ H ₃	CH(Et) ₂	<i>P2₁/c</i>	4	8.946	25.9	40.7	2.905	—	—	131.6
(f)	BrC ₆ H ₄	Retigeranyl	<i>P2₁</i>	2	9.377	19.3	42.0	3.16	—	—	117.4
(2) Glide type											
(g)	BrC ₆ H ₄	Me	<i>Pna2₁</i>	4	9.70	1.5	5.9	2.904	—	—	164.1
(h)	ClC ₆ H ₄	Me	<i>Pna2₁</i>	4	9.73	1.0	5.5	2.825	—	—	160.6
(i)	MeC ₆ H ₄	Me	<i>Pna2₁</i>	4	9.899	2.6	5.7	2.904	1.97	174	166.9
(j)	Cl ₂ C ₆ H ₃	CH(Me) ₂	<i>P2₁/c</i>	4	9.676	4.7	27.6	2.84	1.85	172	144.8
(k)	C ₁₀ H ₇	OMe	<i>P2₁/c</i>	4	9.883	6.5	66.9	2.861	1.96	168	178.4
(3) Translation type											
(l)	ClC ₆ H ₄	CH(Pr) ₂	<i>P2₁2₁2₁</i>	4	4.972	0.4	39.8	2.869	—	—	176.7
(m)	2-Fluorenyl	Me	<i>Cc</i>	4	4.830	5.4	42.4	2.954	2.01	168	162.1
(n)	4-Fluorenyl	Me	<i>P2₁/n</i>	4	4.770	4.4	48.2	2.868	—	—	165.9

References: (a) Acetanilide (Brown, 1966). (b) *p*-Acetanilide (this work). (c) *N*-2-Naphthylacetamide (this work). (d) *p*-Methylacetanilide, monoclinic form (Haisa, Kashino, Matsuzaki, Kawai & Kunitomi, 1977). (e) 2-Chloro-5-(trifluoromethyl)diethylacetanilide (Cohen-Addad, 1973). (f) Retigeranic acid *p*-bromoanilide (Kaneda, Itaka & Shibata, 1974). (g) *p*-Bromoacetanilide (Andreetti, Cavalca, Domiano & Musatti, 1968). (h) *p*-Chloroacetanilide (Subramanian, 1966). (i) *p*-Methylacetanilide, orthorhombic form (Haisa, Kashino, Matsuzaki, Kawai & Kunitomi, 1977). (j) 3,4-Dichloroisobutyranilide (Precigoux, Busetta & Hospital, 1976). (k) Methyl *N*-(1-naphthyl)carbamate (Service d'Analyse des Structures Cristallines, 1976). (l) 4-Chlorodipropylacetanilide (Cohen-Addad, 1973). (m) *N*-2-Fluorenylacetamide (this work). (n) 4-Acetylaminofluorene (Van Meerssche, Germain, Declercq & Touillaux, 1979).

* *D*: Dimension of the crystallographic axis along which the ribbon of hydrogen bonds extends.

† θ : Angle between the amido plane and the crystallographic axis along which the ribbon extends.

‡ δ : see Table 4.

2.865 (3), H...O 1.96 (3) Å, N—H...O 168 (3)° for NAA] to form a ribbon along **a**. The ribbons are held together by van der Waals interactions between the molecules related by a *c* glide to form a sheet parallel to (001). The sheets related by an *a* glide are stacked along **b** to complete a whole crystal.

In the crystals of FAA, the molecules related by a *b* translation are linked together by an N—H...O hydrogen bond [N...O 2.954 (6), H...O 2.01 (5) Å, N—H...O 168 (5)°] to form a ribbon along **b**. The ribbons are held together by van der Waals interactions between the molecules related by a *c* glide and between those related by *C*-centring to complete a whole crystal.

Morphotropism

Table 5 lists the characteristic features of the crystal structure and the N—H...O=C hydrogen bond of aromatic amides. The crystal structures are classified by the type of the hydrogen-bonded ribbons, whose component molecules are related by a 2_1 axis, a glide plane or translation. Dimensions of the hydrogen bonds are similar among these types. The C=O...N angles tend to decrease linearly with increase in the angle θ between the amido plane and the crystallographic axis

along which the ribbon extends, and the sum of the C=O...N angle and 2θ is nearly 180°, as can be seen from Fig. 3. This means that the deviation of the C=O...N angle from 180° results mainly from the loss of coplanarity of the amido planes linked by the hydrogen bond. Crystals of the translation and 2_1 types obey this rule, except (*f*) with a bulky substituent. This is not the case for the glide type where the amido planes deviate from the parallel alignment to the glide plane.

Acetanilide (*a*), a prototype of the aromatic amide, AAS (*b*) and NAA (*c*) belong to the 2_1 type, their space groups being *Pbca*. Sheets of the ribbons are formed by the interactions between the aromatic rings related by the glide plane perpendicular to the 2_1 axis. The dihedral angles of 66.6° for (*a*) and 75.3° for (*b*) between the rings are comparable with that in benzene (85°), and that of 54.0° for (*c*) is comparable to that of naphthalene (52°). The values are approximately equal to $2(\theta + \delta)$, indicating that the aromatic exocyclic C—N bonds are nearly parallel to the glide plane.

Descent to the space group *P2₁/c* (*d*) is caused by 4-methyl substitution on the phenyl ring of (*a*), because the intersheet interactions would be unfavourable owing to the bulkiness of the substituent. However, the dihedral angle between the rings remains 66.7° as in (*a*), an elimination of 2_1 along **b** of (*a*) resulting in the

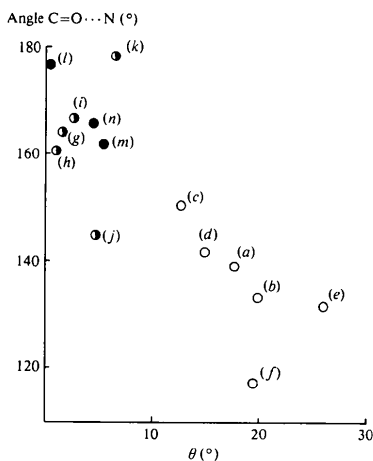


Fig. 3. Plot of the C=O...N angle (°) vs the angle θ (°) for respective types of hydrogen bonds of *N*-aromatic amides: \circ 2_1 type, \bullet glide type and \blacklozenge translation type. The definition of θ and references for the compounds are given in Table 5.

structure of (*d*). A similar situation has been found in the descent from *Pbca* to *P2₁/c* for pyrrolidinium 4-substituted benzoates (Kashino, Kataoka & Haisa, 1978).

On the other hand, in (*e*) the glide interaction disappears as an effect of the 2-chloro-5-trifluoromethyl substitution. The sheets are formed between the molecules related by an *a* translation. Nevertheless, the space group still remains *P2₁/c*, since the sheets are stacked by $\bar{1}$. The bulky asymmetric compound (*f*) crystallizes in a lower enantiomorphic space group.

Crystals of (*g*), (*h*) and (*i*) are isotypic (*Pna2₁*) and belong to the glide type. Occurrence of the dimorphs (*d*) and (*i*) shows that both the 2_1 and the glide types are probable for the same anilides. In the 2_1 type the angle between the long axes of the hydrogen-bonded molecules projected along the 2_1 axis is restricted to 180° , while in the glide type the corresponding angle may take an arbitrary value favourable for the packing of the ribbons. In this sense, the freedom for packing is greater for the glide type than the 2_1 type. Thus, the glide type may be chosen by a rather complicated Ar or *R* as in (*j*) and (*k*).

The crystals of (*l*), (*m*) and (*n*) are of the translation type. In this type the ribbon is stabilized by the parallel stacking of the aromatic rings. This type seems to occur when a dimension of Ar or *R* is large. The δ for the translation type ranges from 39 to 48° , the calculated δ being 42.8° for a geometry where $N\cdots O$ is 2.90 Å, $C=O\cdots N = 180^\circ$, $\theta = 0^\circ$ and the interplanar distance between the stacking rings is 3.40 Å.

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