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N-Acetyl-L-phenylalanine-*N*-methylamide

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Abstract. L-APhe*N*MA, $C_{12}H_{16}N_2O_2$, $M_r = 220{\cdot}2$, monoclinic, $P2_1$, $a = 11{\cdot}695\,(1)$, $b = 4{\cdot}966\,(1)$, $c = 11{\cdot}531\,(1)$ Å, $\beta = 116{\cdot}6\,(1)°$, $Z = 2$, $D_x = 1{\cdot}215$ g cm^{-3}. The conformation of the molecule and the crystal packing closely resemble those of DL-APhe*N*MA. The torsion angles' φ_{CN} and ψ_{CC} are

Table 1. *Final atomic parameters for N-acetyl-L-phenylalanine-N-methylamide*

$T = \exp[-(\beta_{11}h^2 + \cdots + 2\beta_{23}kl)]$. All quantities are $\times 10^4$

	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	10905 (6)	3097 (0)	1803 (7)	69 (6)	410 (37)	133 (9)	−10 (13)	36 (6)	2 (16)
C(2)	9579 (6)	2096 (14)	1371 (6)	98 (7)	309 (29)	84 (7)	22 (13)	34 (6)	2 (15)
C(3)	7304 (6)	3298 (13)	516 (6)	84 (6)	270 (32)	117 (8)	26 (12)	42 (6)	43 (14)
C(4)	6637 (5)	3819 (15)	−936 (6)	67 (6)	314 (27)	127 (8)	−10 (14)	42 (6)	8 (15)
C(5)	5749 (7)	1979 (19)	−3139 (6)	179 (11)	493 (41)	90 (8)	−10 (19)	53 (8)	−22 (18)
C(6)	6675 (6)	4919 (16)	1201 (6)	89 (7)	443 (36)	119 (9)	28 (15)	37 (6)	60 (16)
C(7)	7251 (6)	4394 (15)	2651 (6)	84 (6)	403 (37)	135 (9)	53 (14)	52 (6)	73 (17)
C(8)	8262 (7)	5906 (17)	3498 (7)	138 (9)	438 (40)	160 (10)	−33 (18)	81 (8)	−8 (20)
C(9)	8792 (7)	5410 (17)	4835 (7)	143 (9)	488 (44)	141 (10)	−27 (17)	57 (8)	−3 (18)
C(10)	8321 (7)	3406 (17)	5307 (7)	142 (9)	520 (44)	122 (9)	12 (19)	64 (8)	13 (19)
C(11)	7324 (7)	1877 (19)	4469 (7)	155 (10)	556 (44)	147 (10)	−37 (19)	95 (9)	14 (21)
C(12)	6787 (7)	2334 (17)	3131 (7)	106 (8)	521 (43)	139 (9)	−51 (16)	56 (7)	21 (18)
O(1)	9336 (4)	−338 (9)	1318 (5)	108 (5)	261 (21)	170 (6)	28 (10)	37 (5)	3 (11)
O(2)	6452 (4)	6161 (10)	−1347 (4)	148 (6)	232 (20)	124 (6)	1 (11)	25 (5)	50 (11)
N(1)	8649 (4)	3909 (11)	1006 (5)	75 (5)	226 (21)	118 (6)	−3 (11)	35 (5)	8 (12)
N(2)	6327 (5)	1732 (12)	−1718 (5)	131 (7)	244 (25)	150 (7)	10 (12)	62 (6)	18 (14)

$T = \exp[-B\sin^2\theta/\lambda^2]$. Fractional coordinates are $\times 10^3$.

	x	*y*	*z*	B ($\times 10$ Å^2)		*x*	*y*	*z*	B ($\times 10$ Å^2)
H(Cl)	1106 (7)	515 (19)	171 (7)	117 (24)	H′(C6)	686 (5)	632 (17)	112 (5)	73 (18)
H′(Cl)	1137 (7)	287 (19)	272 (7)	108 (25)	H(C8)	867 (6)	740 (18)	319 (6)	80 (21)
H″(Cl)	1116 (7)	246 (22)	145 (7)	125 (25)	H(C9)	957 (6)	650 (20)	538 (6)	82 (19)
H(C3)	723 (5)	107 (14)	73 (5)	55 (15)	H(C10)	871 (6)	301 (16)	634 (6)	72 (20)
H(C5)	574 (7)	31 (20)	−345 (7)	121 (29)	H(C11)	689 (5)	45 (14)	473 (5)	73 (18)
H′(C5)	481 (7)	264 (19)	−353 (7)	106 (24)	H(C12)	593 (7)	172 (22)	249 (7)	108 (25)
H″(C5)	627 (7)	268 (20)	−337 (7)	115 (25)	H(N1)	882 (5)	517 (13)	105 (5)	53 (15)
H(C6)	575 (4)	452 (12)	76 (4)	41 (13)	H(N2)	644 (5)	3 (13)	−143 (5)	53 (16)

−106·7 and 103·8° respectively, which are very close to those given for the pleated-sheet polypeptide structure.

Introduction. L-APhe*N*MA was synthesized from L-acetylphenylalanine by the activated methyl ester method. Crystals were grown from an aqueous solution and one with approximate dimensions 0·015 × 0·14 × 0·5 mm was mounted on a Philips PW 1100 four-circle diffractometer. The θ–2θ scanning technique was employed for the data collection with a scan speed of $2\theta = 4°$ min^{-1}. The scans were repeated twice when the total counts during a scan were less than 10^4. The background was measured at each end of the scan for half the total scan time. 661 unique reflexions were measured as above the $2\sigma(I)$ level with graphite-monochromated Cu$K\alpha$ radiation for 2θ less than 156°; these correspond to 49% of the theoretically possible number of reflexions in the same angular range.

The structure was solved with *MULTAN* (Main, Woolfson & Germain, 1971). The least-squares refinement of the structural parameters was carried out with *ORFLS* (Busing, Martin & Levy, 1962). The following weighting scheme was employed: $\sqrt{w} = 1/\sigma$, where σ is the standard deviation of the structure factor estimated by counting statistics. The final R value was 0·039 for 661 non-zero reflexions.* There was no need to apply absorption or extinction corrections. The atomic parameters are listed in Table 1.

Discussion. The bond lengths and torsion angles are listed in Table 2. The bond lengths and angles are in good agreement with the standard values given for the peptide model (Pauling & Corey, 1953) and also with those found in DL-APhe*N*MA (Harada & Iitaka, 1974). As has been seen in DL-APhe*N*MA, the short C(1)–C(2) distance, 1·488 Å, may be attributed to the librational thermal motions of the terminal C atom, C(1).

The conformations about the C$^\alpha$ atom defined by the torsion angles φ_{CN} and ψ_{CC} are −106·7 and 103·8°, which can be compared with −105·5 and 107·9° in DL-APhe*N*MA, −117 and 109° in *N*-acetyl-DL-methionine-*N*-methylamide (Harada & Iitaka, 1977*a*), −118 and 113° in *N*-acetyl-L-valine-*N*-methylamide (Harada & Iitaka, 1977*b*) and −110 and 113° in the parallel-chain pleated-sheet structure model (PCP model; Pauling & Corey, 1953).

Table 3 shows the deviations of atoms from the least-squares plane calculated for each of the three planar groups. The r.m.s. deviations of the atoms are 0·022 Å for peptide group I, 0·019 Å for peptide group II and 0·004 Å for the phenyl group, which can be compared with 0·012, 0·030 and 0·011 Å, respectively, in DL-APhe*N*MA. The dihedral angle between the two peptide groups is 69·9° (69·2° in DL-APhe*N*MA). The χ angles which define the orientation of the side chain with respect to the main chain are

Table 2. *Bond lengths, angles and torsion angles*

C(1)–C(2)	1·488 (9) Å	N(1)–C(2)–C(1)	117·4 (6)°
C(2)–N(1)	1·311 (8)	C(4)–C(3)–C(6)	110·5 (6)
C(2)–O(1)	1·245 (9)	C(4)–C(3)–N(1)	109·2 (5)
C(3)–C(4)	1·521 (9)	C(6)–C(3)–N(1)	112·1 (6)
C(3)–C(6)	1·530 (11)	O(2)–C(4)–C(3)	119·8 (6)
C(3)–N(1)	1·447 (8)	O(2)–C(4)–N(2)	122·3 (6)
C(4)–O(2)	1·245 (9)	C(3)–C(4)–N(2)	117·8 (6)
C(4)–N(2)	1·319 (9)	C(7)–C(6)–C(3)	113·4 (6)
C(5)–N(2)	1·472 (9)	C(8)–C(7)–C(6)	120·3 (7)
C(6)–C(7)	1·521 (10)	C(8)–C(7)–C(12)	119·3 (7)
C(7)–C(8)	1·375 (9)	C(6)–C(7)–C(12)	120·3 (7)
C(7)–C(12)	1·388 (12)	C(9)–C(8)–C(7)	120·0 (8)
C(8)–C(9)	1·404 (11)	C(10)–C(9)–C(8)	120·5 (8)
C(9)–C(10)	1·367 (13)	C(11)–C(10)–C(9)	119·7 (8)
C(10)–C(11)	1·368 (10)	C(12)–C(11)–C(10)	120·6 (7)
C(11)–C(12)	1·401 (10)	C(7)–C(12)–C(11)	119·8 (6)
		C(2)–N(1)–C(3)	125·0 (6)
		C(4)–N(2)–C(5)	123·0 (6)

φ	τ[C(4)–C(3)–N(1)–C(2)]	−106·7°
ψ	τ[N(2)–C(4)–C(3)–N(1)]	103·8
ω_1	τ[C(3)–N(1)–C(2)–C(1)]	177·7
ω_2	τ[C(3)–C(4)–N(2)–C(5)]	−176·3
χ^1	τ[C(7)–C(6)–C(3)–N(1)]	−60·9
χ^{21}	τ[C(8)–C(7)–C(6)–C(3)]	89·8
χ^{22}	τ[C(12)–C(7)–C(6)–C(3)]	−88·3

Table 3. *Least-squares planes through planar groups*

X, Y and Z are the orthogonal coordinates measured in Å with $X \| a^*$, $Y \| b$ and $Z \| c$.

(1) Peptide group I

$$0{\cdot}1001X - 0{\cdot}0189Y + 0{\cdot}9948Z = -2{\cdot}456$$

C(1)	−0·025 Å	O(1)	0·008 Å
C(2)	0·039	N(1)	−0·012
C(3)	−0·011		

(2) Peptide group II

$$0{\cdot}8996X + 0{\cdot}0288Y - 0{\cdot}4358Z = 8{\cdot}306$$

C(3)	0·021Å	O(2)	0·002 Å
C(4)	−0·022	N(2)	−0·021
C(5)	0·021		

(3) Benzene ring

$$-0{\cdot}6467X + 0{\cdot}6413Y + 0{\cdot}4128Z = -3{\cdot}809$$

C(6)	0·001Å	C(10)	0·002 Å
C(7)	0·009	C(11)	0·003
C(8)	−0·005	C(12)	−0·009
C(9)	−0·001		

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32033 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Comparison of* χ *angles found in the derivatives of phenylalanine*

Compound	χ^1	χ^{21}	χ^{22}	Reference
Phenylalanine.HCl	62·1°	83·6°	−97·6°	(1)
	172·0	83·6	−93·1	
Gly-Phe-Gly	185·3	102·5	−81·5	(2)
L-APhe*N*MA	−60·9	89·6	−88·3	(3)
DL-APhe*N*MA	−57·4	87·4	−93·2	(4)
N-Chloroacetyl-L-Phe-	−175	89	−92	(5)
L-Phe-ethyl ester	−71	96	−92	
N-Bromoacetyl-L-Phe-	−177	97	−89	
L-Phe-ethyl ester	−64	92	−90	

References: (1) Lakshminarayanan, Sasisekharan & Ramachandran (1967). (2) Marsh & Glusker (1961). (3) Present study. (4) Harada & Iitaka (1974). (5) Wei, Doherty & Einstein (1972).

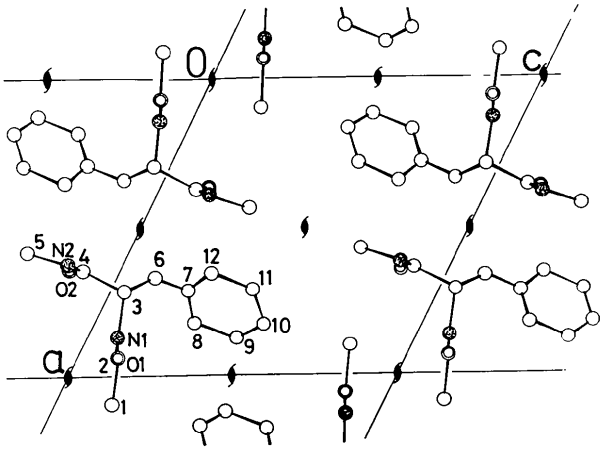

Fig. 1. The projection of the crystal structure along the *b* axis.

listed in Table 4 for comparison with those reported for various phenylalanine derivatives. All the χ angles found in L-APhe*N*MA and DL-APhe*N*MA are very close to each other, reflecting the close similarity in the crystal structures. It may be seen in Table 4 that all the three possible conformations about the C^{α}–C^{β} bond have been found in the phenylalanine residues.

The projection of the crystal structure along the *b* axis is shown in Fig. 1. As indicated by the similarity in the cell dimensions, $b = 4{\cdot}966$ Å ($b = 4{\cdot}98$ Å in DL-APhe*N*MA) and $a = 11{\cdot}695$ Å ($c = 12{\cdot}29$ Å in DL-APhe*N*MA), the arrangement of molecules in (001) is very similar to that in (100) of DL-APhe*N*MA [Fig. 1 can be compared with Fig. 3 in the preceding paper (Harada & Iitaka, 1974)].

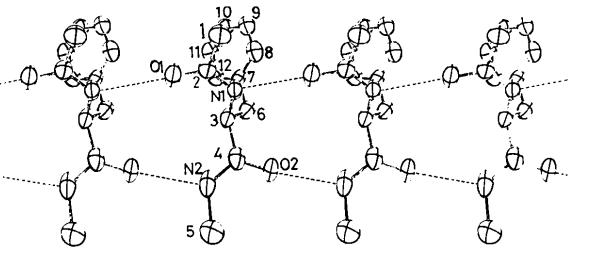

Fig. 2. A view of the molecules bound together by hydrogen bonds to form a belt structure.

Table 5. *Interatomic distances and angles associated with the hydrogen bonds*

Symmetry code: (i) $x, 1+y, z$; (ii) $x, -1+y, z$.

	N(1)···O(1^{i})	N(2)···O(2^{ii})
	2·963 (7) Å	2·810 (8) Å
∠(O=C···N)	2·7 (3)°	8·4 (3)°
∠(C=O···N)	176·2 (5)	167·9 (5)

The sheet structure, as depicted in Fig. 2 (Fig. 4 in the preceding paper), is also found to extend along the *b* axis. Within the sheet, the molecules are parallel and linked together by hydrogen bonds. The interatomic distances and angles associated with the hydrogen bonds are shown in Table 5. The lengths of the hydrogen bonds, 2·810 and 2·963 Å, are very close to those found in DL-APhe*N*MA (2·80 and 2·95 Å).

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