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N-Acetyl-DL-tryptophan-*N*-methylamide

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Abstract. $C_{14}H_{17}N_3O_2$, $M_r = 259{\cdot}3$, monoclinic, $P2_1/a$, $a = 14{\cdot}023$ (7), $b = 11{\cdot}896$ (6), $c = 9{\cdot}105$ (5) Å, $\beta = 107{\cdot}0$ (1)°, $Z = 4$, $D_x = 1{\cdot}186$ g cm^{-3}. The structure was solved by direct methods and refined to an R value of 0·049. The conformation of the molecule about the two peptide linkages is $\varphi_{CN} = -103{\cdot}7°$ and $\psi_{CC} = 141{\cdot}4°$ for L-molecules, and is consistent with that of the β-structure of polypeptides. The molecules are bound together through hydrogen bonds to form a sheet.

Introduction. The compound was synthesized by one of the authors (YH) by means of the DCC (*N*,*N*′-dicyclohexylcarbodiimide) method (Sheehan & Hess, 1955). The crystals were grown from an ethanol solution. A crystal, approximately 0·08 × 0·45 × 0·62 mm, was mounted on a Philips PW 1100 four-circle diffractometer. The intensity data were collected by the θ–2θ scanning technique with a 2θ scan speed of 4° min^{-1} and graphite-monochromated Cu $K\alpha$ radiation. 2347 unique reflexions, 82% of the theoretically possible number of reflexions, were measured within 2θ less than 156° as being above the $2\sigma(I)$ level.

The structure was solved with *MULTAN* (Main, Woolfson & Germain, 1971) and least-squares refinement of the structural parameters was carried out with *ORFLS* (Busing, Martin & Levy, 1962).

In the refinement process the eight strongest reflex-

Table 1. *Atomic parameters for N-acetyl-*DL*-tryptophan-N-methylamide*

For C, O and N, $T = \exp[-(\beta_{11}h^2 + \cdots + 2\beta_{23}kl)]$; all quantities are $\times 10^4$. For H, $T = \exp[-B \sin^2\theta/\lambda^2]$; fractional coordinates are $\times 10^3$, B is $\times 10$ Å^2.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	5223 (3)	−2780 (3)	8529 (4)	130 (3)	74 (3)	217 (6)	−17 (2)	77 (4)	−46 (3)
C(2)	5082 (2)	−1784 (2)	7470 (3)	54 (2)	61 (2)	132 (4)	3 (1)	26 (2)	−9 (2)
C(3)	4632 (2)	215 (2)	7187 (3)	56 (2)	55 (2)	98 (4)	0 (1)	27 (2)	−1 (2)
C(4)	5495 (2)	1002 (2)	7924 (3)	52 (2)	67 (2)	112 (4)	−2 (1)	33 (2)	−3 (2)
C(5)	6614 (3)	2453 (3)	7482 (5)	71 (2)	105 (3)	257 (7)	29 (2)	46 (3)	−19 (4)
C(6)	3640 (2)	733 (2)	7252 (3)	52 (2)	65 (2)	161 (5)	1 (2)	26 (2)	16 (3)
C(7)	2758 (2)	48 (2)	6388 (4)	53 (2)	61 (2)	177 (5)	4 (2)	29 (2)	6 (3)
C(8)	2242 (3)	−708 (3)	6971 (4)	76 (2)	87 (3)	215 (6)	12 (2)	43 (3)	−7 (4)
C(9)	1529 (2)	−737 (3)	4427 (4)	56 (2)	60 (2)	238 (6)	5 (2)	19 (3)	10 (3)
C(10)	944 (3)	−943 (3)	2914 (5)	66 (2)	74 (3)	284 (8)	3 (2)	−8 (3)	35 (4)
C(11)	1177 (3)	−375 (3)	1766 (5)	94 (3)	96 (3)	219 (7)	−15 (3)	−18 (4)	29 (4)
C(12)	1960 (3)	399 (4)	2055 (4)	102 (3)	112 (4)	186 (6)	−6 (3)	13 (4)	−9 (4)
C(13)	2531 (2)	613 (3)	3543 (4)	70 (2)	84 (3)	188 (5)	6 (2)	21 (3)	−3 (3)
C(14)	2321 (2)	46 (2)	4751 (4)	50 (2)	58 (2)	186 (5)	3 (1)	21 (2)	5 (3)
O(1)	5267 (2)	−1851 (2)	6220 (2)	79 (1)	71 (2)	137 (3)	−13 (1)	48 (2)	−6 (2)
O(2)	5862 (2)	1049 (2)	9326 (2)	76 (1)	130 (2)	103 (3)	32 (2)	27 (2)	6 (2)
N(1)	4781 (2)	−854 (2)	7985 (2)	67 (2)	62 (2)	105 (3)	−3 (1)	34 (2)	−12 (2)
N(2)	5802 (2)	1643 (2)	6962 (3)	60 (1)	75 (2)	135 (3)	7 (1)	33 (2)	−15 (2)
N(3)	1491 (2)	−1188 (2)	5793 (4)	73 (2)	84 (2)	276 (6)	26 (2)	38 (3)	−5 (3)

	x	y	z	B		x	y	z	B
H(C1)	502 (3)	−341 (4)	794 (5)	81 (11)	H(C8)	235 (3)	−94 (3)	803 (4)	83 (10)
H′(C1)	493 (3)	−267 (3)	936 (5)	90 (11)	H(C10)	39 (3)	−146 (3)	279 (4)	89 (10)
H″(C1)	593 (4)	−289 (4)	899 (5)	113 (16)	H(C11)	82 (3)	−48 (4)	70 (5)	98 (11)
H(C3)	463 (2)	7 (2)	610 (3)	36 (5)	H(C12)	211 (3)	80 (3)	118 (4)	87 (10)
H(C5)	647 (4)	304 (5)	820 (7)	136 (18)	H(C13)	308 (2)	119 (3)	373 (4)	68 (8)
H′(C5)	721 (4)	211 (5)	820 (7)	134 (19)	H(N1)	465 (2)	−86 (3)	890 (3)	55 (7)
H″(C5)	671 (2)	280 (3)	668 (4)	133 (8)	H(N2)	552 (4)	157 (5)	600 (6)	59 (18)
H(C6)	358 (2)	152 (3)	682 (3)	51 (7)	H(N3)	107 (3)	−177 (4)	601 (5)	110 (13)
H′(C6)	366 (2)	78 (3)	838 (4)	55 (7)					

ions were excluded because of their large discrepancies between observed and calculated intensities. The following weighting scheme was applied: $\sqrt{w} = 1{\cdot}0$ for $|F_o| \leq 30{\cdot}0$, $\sqrt{w} = 30{\cdot}0/|F_o|$ for $|F_o| > 30{\cdot}0$.

The atomic scattering factors used for C, N and O atoms were those cited in *International Tables for X-ray Crystallography* (1962). The final R value was 0·049 for 2339 non-zero unique reflexions.* The atomic parameters are listed in Table 1.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32060 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1, 1NZ, England.

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)–C(2)	1·504 (5)	O(1)–C(2)–C(1)	120·9 (3)
C(2)–O(1)	1·242 (4)	O(1)–C(2)–N(1)	123·7 (3)
C(2)–N(1)	1·318 (4)	C(1)–C(2)–N(1)	115·4 (3)
C(3)–C(4)	1·522 (4)	C(4)–C(3)–C(6)	110·3 (2)
C(3)–C(6)	1·539 (4)	C(4)–C(3)–N(1)	109·9 (2)
C(3)–N(1)	1·448 (3)	C(6)–C(3)–N(1)	109·4 (2)
C(4)–O(2)	1·230 (3)	O(2)–C(4)–C(3)	121·5 (2)
C(4)–N(2)	1·325 (4)	O(2)–C(4)–N(2)	122·8 (3)
C(5)–N(2)	1·461 (4)	C(3)–C(4)–N(2)	115·7 (2)
C(6)–C(7)	1·497 (4)	C(7)–C(6)–C(3)	112·2 (2)
C(7)–C(8)	1·356 (5)	C(8)–C(7)–C(6)	127·5 (3)
C(7)–C(14)	1·436 (4)	C(8)–C(7)–C(14)	106·9 (3)
C(8)–N(3)	1·387 (4)	C(6)–C(7)–C(14)	125·6 (3)
C(9)–C(10)	1·403 (5)	N(3)–C(8)–C(7)	110·0 (3)
C(9)–C(14)	1·412 (4)	C(10)–C(9)–C(14)	121·2 (3)
C(9)–N(3)	1·369 (5)	C(10)–C(9)–N(3)	131·0 (3)
C(10)–C(11)	1·363 (7)	C(14)–C(9)–N(3)	107·8 (3)
C(11)–C(12)	1·397 (6)	C(11)–C(10)–C(9)	117·6 (4)
C(12)–C(13)	1·380 (5)	C(12)–C(11)–C(10)	122·3 (4)
C(13)–C(14)	1·394 (5)	C(13)–C(12)–C(11)	120·3 (4)
		C(14)–C(13)–C(12)	119·3 (3)
		C(2)–N(1)–C(3)	124·9 (2)
		C(4)–N(2)–C(5)	122·6 (3)
		C(8)–N(3)–C(9)	108·6 (3)
		C(7)–C(14)–C(9)	106·8 (3)
		C(7)–C(14)–C(13)	133·9 (3)
		C(9)–C(14)–C(13)	119·3 (3)

Table 3. *Least-squares planes*

$X \| a^*$, $Y \| b$ and $Z \| c$; X, Y, Z and D are measured in Å.

(1) Peptide group I (acetyl side)

$$0{\cdot}9521X + 0{\cdot}2572Y + 0{\cdot}1655Z = 6{\cdot}734$$

C(1)	0·012 Å	O(1)	0·002 Å
C(2)	−0·013	N(1)	−0·014
C(3)	0·013		

(2) Peptide group II (methylamide side)

$$-0{\cdot}6563X + 0{\cdot}7077Y + 0{\cdot}2615Z = -2{\cdot}687$$

C(3)	0·005 Å	O(2)	0·003 Å
C(4)	−0·009	N(2)	−0·001
C(5)	0·003		

(3) Indole ring

$$-0{\cdot}6245X + 0{\cdot}7309Y + 0{\cdot}2752Z = -0{\cdot}992$$

C(6)	−0·013 Å	C(11)	−0·010 Å
C(7)	0·013	C(12)	−0·010
C(8)	−0·008	C(13)	0·007
C(9)	0·007	C(14)	0·016
C(10)	0·005	N(3)	−0·007

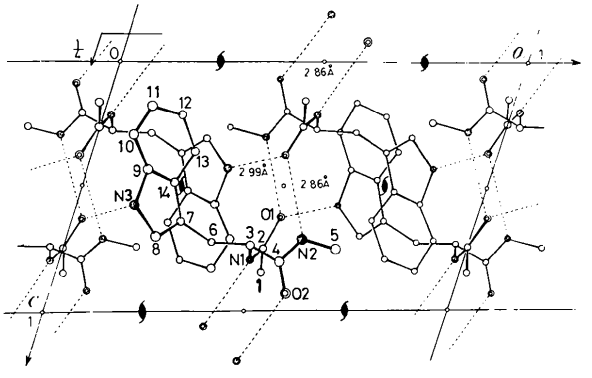

Fig. 1. The projection of the crystal structure along the *b* axis.

Table 4. *Torsion angles* (°) *in tryptophan derivatives*

$\varphi = \tau$[C(4)–C(3)–N(1)–C(2)], $\psi = \tau$[N(2)–C(4)–C(3)–N(1)], $\chi^1 = \tau$[C(7)–C(6)–C(3)–N(1)], $\chi^{21} = \tau$[C(8)–C(7)–C(6)–C(3)], $\chi^{22} = \tau$[C(14)–C(7)–C(6)–C(3)].

Compound	φ	ψ	χ^1	χ^{21}	χ^{22}	References
Present compound	−103·7	141·4	−65·3	98·7	−78·9	
L-Tryptophan.HBr	–	–	65·9	80·7	−106·7	Takigawa *et al.* (1966)
Gly-L-Trp.$2H_2O$	−73·0	(156·4)*	−65·9	60·6	−122·3	Pasternak (1956)
5-Hydroxy-DL-Trp	–	–	−74·8	110·7	–	Wakahara *et al.* (1973)
Acetyl-L-Trp-methyl ester	−65·6	(157·3)*	172·6	87·8	–	Cotrait & Barrans (1974)
Formyl-DL-Trp	–	–	−174·6	105·1	–	Bye, Mostad & Rømming (1973)
Acetyl-L-Trp-monomethylammonium	−85·3	(138·4)*	−174·4	−112·1	67·1	Harada & Iitaka (1977)
Antiparallel-chain pleated sheet	−145	142				Pauling & Corey (1953)
Polyglycine II	−77	145				Crick & Rich (1955)

* The ψ values in parentheses denote that for these compounds, C(4) and N(2) do not belong to the amide groups but to carboxyl groups. Therefore, N(2) is replaced by a C atom.

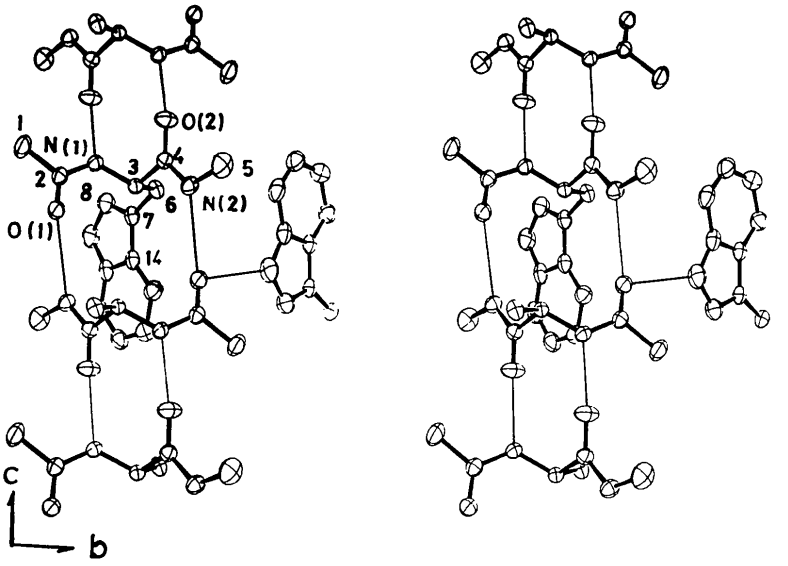

Fig. 2. Stereoscopic view of the molecules plotted by *ORTEP* (Johnson, 1965). The molecules are bound together by hydrogen bonds along the *c* axis to form a belt structure.

Table 5. *Distortions in hydrogen bonds*

Symmetry code: (i) $1-x, -y, 1-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (iii) $1-x, -y, 2-z$.

	$O(1)\cdots N(2^{i})$	$O(1)\cdots N(3^{ii})$	$O(2^{iii})\cdots N(1)$
	2·853 (4) Å	2·989 (4) Å	2·855 (4) Å
∠(O=C···N)	30·0 (2)°	45·8 (2)°	29·6 (2)°
∠(C=O···N)	137·4 (2)	116·8 (2)	138·1 (2)

Discussion. Table 2 lists bond distances and angles. The values are normal and agree well with the standard values for peptides. The planarities of the two peptide groups and indole ring are shown in Table 3. The conformation of the molecule is described by the various torsion angles given in Table 4. The φ and ψ values fall in the region of the β-structure in the Ramachandran plot, but they deviate from the values of the ideal pleated-sheet structure to those of polyglycine II. The three χ angles which define the orientation of the side chain with respect to the main chain are compared in Table 4 with those found in other tryptophan derivatives.

As seen in Table 4, all of the three possible conformations about the $C^{\alpha}-C^{\beta}$ bond, (+)-*gauche*, (−)-*gauche* and *trans*, have been found in these compounds. The χ^{21} angles of most of these tryptophan derivatives lie in the range 60 to 112°. An exception is found in *N*-acetyl-L-tryptophan monomethylammonium in which the χ^{21} angle is −112° and the orientation of the long axis of the indole ring with respect to C^{α} is almost reversed.

The crystal structure along **b** is shown in Fig. 1. As depicted in Fig. 2, the molecules related by a centre of symmetry are laid anti-parallel along **b** and are bound together by the two kinds of hydrogen bond, N(2)H···O(1) and N(1)H···O(2), forming a belt structure. A similar type of hydrogen-bond system was found between the *N*-acetylleucine-*N*-methylamide molecules related by the centre of symmetry (Ichikawa & Iitaka, 1969). These belt structures are arranged to be nearly coplanar in the **b** direction to form a sheet. Besides the hydrogen bonds between adjacent main chains, there is another kind of hydrogen bond connecting the side chain to the neighbouring main chain. The side-chain indole rings extending from the neighbouring sheet are hydrogen-bonded to the carbonyl O atoms of the neighbouring main chains and are stacked along the diad screw axis, filling spaces between the sheets. The distances and angles associated with the hydrogen bonds are tabulated in Table 5.

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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)