torsion angle C(2)–C(1)–C(9)–O(10) is −116·2 (3), which again is similar to the values observed for the 12-membered alkaloids [*e.g.* jacobine −106° and swazine −108° (Laing & Sommerville, 1972)]. In 11-membered PA's, where the ester carbonyl groups are synparallel, the value of this torsion angle ranges from −63 to −88°.

The shortest transannular distances are O(10)···O(15) 2·847 (2) and O(10)···C(14) 2·867 (3) Å, which are comparable with the equivalent distances O(10)···O(16) 2·83 and O(10)···C(15) 2·83 Å in trichodesmine.

The chemical-shift difference ($\Delta\delta$) of 1·34 between the protons at C(9) for the ten-membered pyrrolizidine alkaloid analogue is similar to values reported for 12-membered diesters of (+)-retronecine, but is much higher than the values recorded for 11-membered alkaloids ($\Delta\delta$ 0–0·92), with the exception of dicrotaline ($\Delta\delta$ 1·24) (Brown, Devlin & Robins, 1983). Correlations between the position of the C(9) H atoms and the chemical shift in the NMR spectra have already been discussed (Stoeckli-Evans & Crout, 1976). The large chemical-shift differences arise when one of the C(9) H atoms lies close to both the plane of the unsaturated ring and the plane of the ester group, resulting in a large deshielding effect. The proximity of H(91) to both these planes can be derived from the torsion angles H(91)–C(9)–O(10)–C(11) −46 (3) and H(91)–C(9)–C(1)–C(2) 6·9 (3)°.

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Structure of Boc-Pro-Met-Gly-OBzl,* $C_{24}H_{35}N_3O_6S$

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Abstract. $M_r = 493·6$, monoclinic, $P2_1$, $a = 9·683$ (4), $b = 35·038$ (13), $c = 9·113$ (4) Å, $\beta = 118·6$ (1)°, $V = 2714·5$ Å^3, $Z = 4$, $D_m = 1·18$, $D_x = 1·21$ g cm^{-3}, λ(Cu $K\alpha_1$) = 1·5405 Å, μ(Cu $K\bar{\alpha}$) = 13·05 cm^{-1}, $F(000) = 1008$, $T = 293$ K, $R = 0·061$ for 3328 reflections with $|F_o| > \sigma(F)$. Two crystallographically independent peptide molecules which are related to each other by a pseudo twofold axis are in an extended form. They are alternately arranged to form an infinitely extended ribbon of an antiparallel β sheet. The mean torsion angles φ,ψ of the central Met are −136, 138°, and the hydrogen-bond length is 2·888 Å. A comparison of the Met side chains in related peptides shows that the preferred values are: $\chi^1 = \pm 60°$, $\chi^2 = 180°$, and $\chi^3 = 180°$ or $\pm 60°$.

Introduction. The systematic structural study of a sequentially related oligopeptide is of significance for the elucidation of a sequence–structure relation of peptide chains. Several oligopeptides with a Boc-Pro-*X*-Gly-*Y* sequence, where *X* is any amino acid and *Y* is OH, NH_2, or benzyl ester, have been studied by the X-ray method (Ashida, Tanaka, Yamane & Kakudo, 1981; Ashida, Tanaka & Yamane, 1981). In these peptides, β turns, antiparallel β sheets and poly-

* *N*-(*tert*-Butoxycarbonyl)-L-prolyl-L-methionylglycine benzyl ester.

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(L-proline)II type helices have been found. In Boc-Met-Gly-OBzl, the precursor of the present peptide, a parallel β-sheet structure was observed (Yamane, Umemura, Kojima, Yamada & Ashida, 1980). The present study was undertaken to examine the effect of Met on the structures of peptides.

Experimental. The peptide, m.p. 375–377 K, was synthesized by step-wise elongation from the C terminus. Very thin needle crystal 0·4 × 0·1 × 0·01 mm from a water–methanol solution, D_m by flotation in an *n*-hexane–chloroform solution. Rigaku AFC diffractometer, graphite monochromator, cell constants from 13 reflections. Intensity-data collection: max. 2θ 110°, ω–2θ scan, scan range $\Delta\omega = 1{\cdot}20° + 0{\cdot}142°\tan\theta$, h 0 to 10, k 0 to 36, l −9 to 8, Lp correction, absorption ignored. 3 standard reflections monitored every 50 reflections showed no significant variation in intensity. 3479 unique reflections collected, 3328 with $|F_o| > \sigma(F)$ used for structure determination. Structure solved by the direct method [*MULTAN*78 (Main, Lessinger, Woolfson, Germain & Declercq, 1978)]. Block-diagonal least-squares refinement [*HBLS* VI (Ashida, 1981)], non-hydrogen atoms with anisotropic temperature factors, H atoms found on the difference density map fixed at the geometrically located sites with isotropic temperature factors equal to B_{eq} of the carrier atoms. $\sum w(\Delta F)^2$ minimized, $w = 1{\cdot}0/[\sigma^2(F) + 0{\cdot}0025F_o^2]$; $R = 0{\cdot}061$, $wR = 0{\cdot}080$, $S = 1{\cdot}25$, $(\Delta/\sigma)_{max} = 0{\cdot}09$ in the final refinement cycle, max. peak 0·4 e Å^{-3} in the final difference map. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974), calculations on a FACOM M382 of Nagoya University.

Discussion. Final parameters of the non-hydrogen atoms are listed in Table 1.* The numbering scheme is shown in Fig. 1. Two crystallographically independent molecules *A* and *B* related by a pseudo twofold rotation axis are shown in an *ORTEP* drawing (Johnson, 1965) in Fig. 2. They show a good conformational similarity with each other, one apparent difference being in the orientations of the phenyl groups. The conformational angles are compared in Fig. 1. The bond distances and angles of the two molecules are not significantly different from each other and thus the mean values are listed in Table 2. One anomaly is the unusually short bond distances of S–C(14), 1·710 and 1·507 Å. This suggests the possibility of a disordered structure; however, no indication could be found in the electron density maps.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond lengths and angles of individual molecules, and hydrogen bonds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42009 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structural features of the Boc group conform to those described by Ashida, Tanaka, Shimonishi & Kakudo (1977). The planarity of the Boc-Pro amide group is poor in both molecules, ω deviates considerably from the ideal *cis* form ($\omega = 0°$), and N(1*A*)

Table 1. *Atomic coordinates* (×10⁴) *and* B_{eq} (Å² × 10) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_{j\geq i}\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Molecule *A*				
S(1*A*)	9410 (3)	1000 (1)	14000 (2)	76 (1)
C(1*A*)	8188 (12)	2144 (3)	12428 (10)	87 (4)
C(2*A*)	10165 (10)	2130 (4)	11369 (14)	108 (6)
C(3*A*)	8338 (12)	2705 (2)	10836 (13)	87 (4)
C(4*A*)	8529 (8)	2278 (2)	11044 (9)	61 (3)
C(5*A*)	7191 (7)	2139 (2)	8065 (8)	48 (2)
C(6*A*)	5153 (6)	1629 (2)	7185 (7)	38 (2)
C(7*A*)	3767 (7)	1553 (2)	5455 (8)	56 (3)
C(8*A*)	4442 (9)	1641 (2)	4311 (8)	66 (3)
C(9*A*)	5630 (8)	1966 (2)	5120 (8)	57 (3)
C(10*A*)	6286 (6)	1292 (1)	7879 (6)	35 (2)
C(11*A*)	6675 (6)	652 (2)	9085 (7)	39 (2)
C(12*A*)	7437 (7)	645 (2)	10946 (8)	51 (2)
C(13*A*)	8480 (8)	988 (2)	11752 (8)	60 (3)
C(14*A*)	7814 (14)	1069 (5)	14300 (14)	118 (7)
C(15*A*)	5651 (6)	306 (2)	8354 (7)	38 (2)
C(16*A*)	5446 (7)	−324 (2)	7196 (8)	47 (2)
C(17*A*)	5030 (7)	−569 (2)	8272 (7)	44 (2)
C(18*A*)	3476 (9)	−1107 (2)	8116 (9)	61 (3)
C(19*A*)	2721 (8)	−1422 (2)	6874 (9)	54 (3)
C(20*A*)	3607 (10)	−1663 (2)	6433 (14)	86 (4)
C(21*A*)	2875 (12)	−1939 (3)	5238 (13)	88 (4)
C(22*A*)	1291 (11)	−1992 (2)	4474 (11)	77 (4)
C(23*A*)	429 (10)	−1761 (3)	4947 (12)	82 (4)
C(24*A*)	1117 (9)	−1481 (2)	6093 (10)	66 (3)
N(1*A*)	5942 (6)	1950 (1)	6879 (6)	44 (2)
N(2*A*)	5725 (5)	997 (1)	8353 (5)	36 (2)
N(3*A*)	6325 (5)	12 (1)	7992 (6)	41 (2)
O(1*A*)	7312 (5)	2083 (1)	9573 (5)	52 (2)
O(2*A*)	8047 (6)	2343 (1)	7766 (6)	66 (2)
O(3*A*)	7584 (4)	1296 (1)	7958 (5)	44 (1)
O(4*A*)	4290 (4)	290 (1)	8142 (5)	49 (2)
O(5*A*)	5545 (6)	−545 (1)	9746 (6)	68 (2)
O(6*A*)	3976 (5)	−825 (1)	7306 (5)	52 (2)
Molecule *B*				
S(1*B*)	3737 (4)	427 (1)	14043 (3)	110 (2)
C(1*B*)	2485 (17)	−745 (5)	12404 (14)	123 (7)
C(2*B*)	−417 (15)	−795 (4)	11263 (14)	112 (6)
C(3*B*)	1105 (13)	−1305 (3)	10649 (13)	96 (5)
C(4*B*)	919 (12)	−885 (2)	10959 (10)	78 (4)
C(5*B*)	−382 (8)	−699 (2)	8049 (9)	57 (3)
C(6*B*)	876 (7)	−176 (2)	7233 (8)	46 (2)
C(7*B*)	702 (8)	−97 (2)	5507 (9)	55 (3)
C(8*B*)	−1033 (9)	−166 (2)	4373 (9)	65 (3)
C(9*B*)	−1439 (8)	−495 (2)	5138 (9)	62 (3)
C(10*B*)	458 (6)	173 (1)	7934 (7)	38 (2)
C(11*B*)	1296 (6)	802 (1)	9191 (7)	40 (2)
C(12*B*)	2490 (8)	807 (2)	11069 (8)	58 (3)
C(13*B*)	2229 (9)	479 (3)	12017 (10)	71 (4)
C(14*B*)	4874 (16)	233 (3)	13594 (12)	109 (6)
C(15*B*)	1579 (6)	1155 (1)	8414 (7)	38 (2)
C(16*B*)	749 (6)	1793 (2)	7390 (8)	46 (2)
C(17*B*)	2136 (7)	2016 (2)	8634 (9)	52 (2)
C(18*B*)	3693 (10)	2565 (2)	8841 (13)	91 (4)
C(19*B*)	3664 (9)	2885 (2)	7779 (14)	87 (4)
C(20*B*)	3553 (16)	2819 (3)	6237 (22)	137 (8)
C(21*B*)	3537 (19)	3126 (4)	5272 (22)	149 (10)
C(22*B*)	3636 (12)	3499 (3)	5870 (21)	135 (7)
C(23*B*)	3761 (16)	3555 (3)	7342 (16)	149 (6)
C(24*B*)	3737 (17)	3256 (3)	8259 (15)	153 (6)
N(1*B*)	−228 (6)	−481 (1)	6920 (6)	46 (2)
N(2*B*)	1472 (5)	459 (1)	8409 (6)	39 (2)
N(3*B*)	569 (5)	1438 (1)	8086 (6)	44 (2)
O(1*B*)	829 (6)	−652 (1)	9546 (6)	61 (2)
O(2*B*)	−1508 (6)	−913 (1)	7647 (7)	73 (2)
O(3*B*)	−753 (5)	186 (1)	8062 (6)	58 (2)
O(4*B*)	2705 (4)	1175 (1)	8113 (5)	47 (2)
O(5*B*)	2987 (6)	1946 (1)	10058 (6)	72 (2)
O(6*B*)	2346 (6)	2318 (1)	7832 (7)	73 (2)

deviates by 0·147 Å from the plane of the three bonded atoms C(5*A*), C(6*A*) and C(9*A*). Such a large distortion has often been found in the *X*-Pro peptide bonds (Ashida, Tanaka, Yamane & Kakudo, 1981). The conformation of the pyrrolidine ring is C_s-C$^\beta$-*exo* (notation of Ashida & Kakudo, 1974) in both molecules. It is to be noted that φ(Pro) 174° is unusually close to 180°, the N–C$^\alpha$–C′–N bond being nearly fully extended.

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

Mean values of molecules *A* and *B* are listed. E.s.d.'s are (Hamilton, 1964): $\sigma(l) = \sigma(A)\sigma(B)/[\sigma^2(A)+\sigma^2(B)]^{0.5}$.

C(1)–C(4)	1·530 (11)	C(13)–S	1·767 (6)
C(2)–C(4)	1·519 (11)	S–C(14)	1·609 (11)
C(3)–C(4)	1·516 (11)	C(11)–C(15)	1·509 (6)
C(4)–O(1)	1·478 (7)	C(15)–O(4)	1·242 (6)
O(1)–C(5)	1·327 (6)	C(15)–N(3)	1·332 (6)
C(5)–O(2)	1·224 (7)	N(3)–C(16)	1·440 (6)
C(5)–N(1)	1·347 (7)	C(16)–C(17)	1·497 (7)
N(1)–C(6)	1·450 (6)	C(17)–O(5)	1·188 (7)
C(6)–C(7)	1·527 (7)	C(17)–O(6)	1·342 (6)
C(7)–C(8)	1·509 (8)	O(6)–C(18)	1·458 (8)
C(8)–C(9)	1·513 (8)	C(18)–C(19)	1·486 (10)
C(9)–N(1)	1·482 (7)	C(19)–C(20)	1·386 (13)
C(6)–C(10)	1·527 (6)	C(20)–C(21)	1·378 (15)
C(10)–O(3)	1·229 (6)	C(21)–C(22)	1·381 (13)
C(10)–N(2)	1·326 (5)	C(22)–C(23)	1·337 (13)
N(2)–C(11)	1·462 (6)	C(23)–C(24)	1·351 (12)
C(11)–C(12)	1·516 (7)	C(24)–C(19)	1·372 (11)
C(12)–C(13)	1·522 (8)		
C(1)–C(4)–C(2)	110·8 (6)	N(2)–C(11)–C(12)	111·9 (4)
C(1)–C(4)–C(3)	109·2 (6)	C(11)–C(12)–C(13)	112·8 (5)
C(1)–C(4)–O(1)	101·8 (6)	C(12)–C(13)–S	114·3 (4)
C(2)–C(4)–C(3)	114·8 (6)	C(13)–S–C(14)	98·6 (5)
C(2)–C(4)–O(1)	109·6 (6)	C(12)–C(11)–C(15)	109·3 (4)
C(3)–C(4)–O(1)	110·0 (6)	C(11)–C(15)–O(4)	121·8 (4)
C(4)–O(1)–C(5)	119·7 (5)	C(11)–C(15)–N(3)	115·8 (4)
O(1)–C(5)–N(1)	110·8 (5)	O(4)–C(15)–N(3)	122·4 (4)
O(1)–C(5)–O(2)	126·6 (5)	C(15)–N(3)–C(16)	121·0 (4)
O(2)–C(5)–N(1)	122·7 (5)	N(3)–C(16)–C(17)	113·4 (4)
C(5)–N(1)–C(6)	126·4 (4)	C(16)–C(17)–O(5)	127·8 (5)
C(5)–N(1)–C(9)	119·7 (4)	C(16)–C(17)–O(6)	108·3 (4)
C(9)–N(1)–C(6)	111·9 (4)	O(5)–C(17)–O(6)	124·0 (5)
N(1)–C(6)–C(10)	110·4 (4)	C(17)–O(6)–C(18)	116·9 (5)
N(1)–C(6)–C(7)	102·9 (4)	O(6)–C(18)–C(19)	107·0 (6)
C(7)–C(6)–C(10)	112·3 (4)	C(18)–C(19)–C(20)	121·0 (7)
C(6)–C(7)–C(8)	102·6 (4)	C(18)–C(19)–C(24)	121·9 (7)
C(7)–C(8)–C(9)	106·1 (5)	C(20)–C(19)–C(24)	117·2 (8)
C(8)–C(9)–N(1)	103·1 (4)	C(19)–C(20)–C(21)	119·7 (9)
C(6)–C(10)–N(2)	115·3 (4)	C(20)–C(21)–C(22)	121·0 (11)
C(6)–C(10)–O(3)	120·8 (4)	C(21)–C(22)–C(23)	118·8 (9)
O(3)–C(10)–N(2)	123·1 (4)	C(22)–C(23)–C(24)	120·8 (8)
C(10)–N(2)–C(11)	122·3 (4)	C(23)–C(24)–C(19)	122·7 (8)
N(2)–C(11)–C(15)	110·0 (4)		

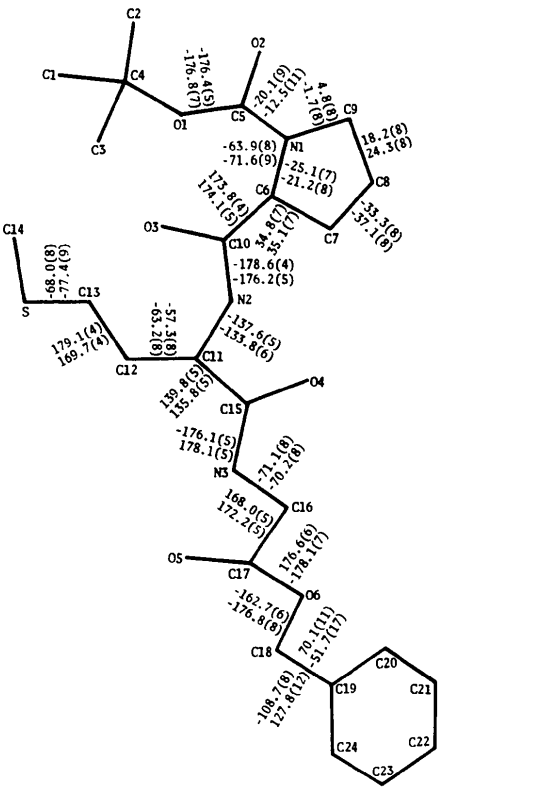

Fig. 1. Atomic numbering scheme, and the principal torsion angles (°) of molecules *A* (upper) and *B* (lower).

Table 3. *Conformations of* Met *side chains* N–C$^\alpha$–C$^\beta$–C$^\gamma$–S$^\delta$–C$^\varepsilon$ *in peptides*

			χ^1	χ^2	χ^3*	Conformation
Acetyl-Met-N(CH$_3$)$_2$		(*a*)	−72	173	−177	$\bar{G}$-*T*-*T*
Acetyl-Met-OMe		(*b*)	−64	178	−179	$\bar{G}$-*T*-*T*
Ala-Met		(*c*)	67	175	−174	*G*-*T*-*T*
Met-Met (Met$_2$)		(*d*)	68	−171	−58	*G*-*T*-$\bar{G}$
Formyl-Met		(*e*)	54	176	174	*G*-*T*-*T*
Boc-Met-Gly-OBzl		(*f*)	−73	175	175	$\bar{G}$-*T*-*T*
Trp-Met-Asp-Phe-NH$_2$	(*A*)	(*g*)	−67	−165	−166	$\bar{G}$-*T*-*T*
	(*B*)		−64	178	81	$\bar{G}$-*T*-*G*
Boc-Pro-Met-Gly-OBzl	(*A*)	(*h*)	−57	179	−68	$\bar{G}$-*T*-$\bar{G}$
	(*B*)		−63	170	−77	$\bar{G}$-*T*-$\bar{G}$
Met-Met (Met$_1$)		(*d*)	−167	−168	178	*T*-*T*-*T*
Met-Glu-His-Phe		(*i*)	−170	176	120	*T*-*T*-*S*†

References: (*a*) Aubry, Marraud, Protas & Néel (1971); (*b*) Geddes, Hamodrakas & Sheldrick (1974); (*c*) Stenkamp & Jensen (1974); (*d*) Stenkamp & Jensen (1975); (*e*) Chen & Parthasarathy (1977); (*f*) Yamane, Umemura, Kojima, Yamada & Ashida (1980); (*g*) Cruse, Egert, Viswamitra & Kennard (1982); (*h*) present study; (*i*) Admiraal & Vos (1983).

* Conformation angles: χ^1(N–C$^\alpha$–C$^\beta$–C$^\gamma$), χ^2(C$^\alpha$–C$^\beta$–C$^\gamma$–S$^\delta$), χ^3(C$^\beta$–C$^\gamma$–S$^\delta$–C$^\varepsilon$).

† *S*: skew, ~120°.

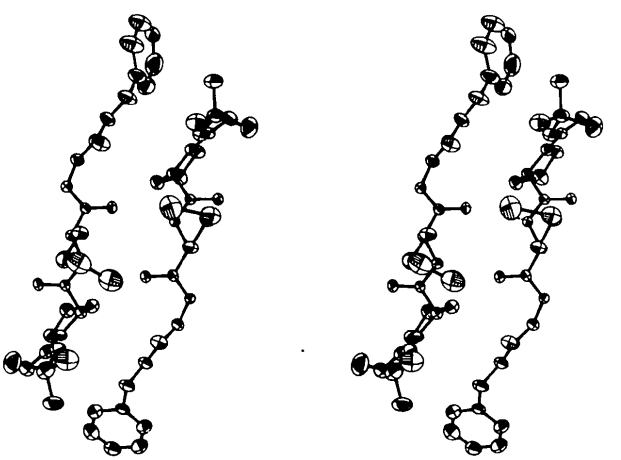

Fig. 2. *ORTEP* (Johnson, 1965) drawing of a pair of independent molecules *A* (right) and *B* (left), which are hydrogen bonded by two (Met)N–H···O=C(Met) bonds.

Table 4. *Structural parameters of antiparallel β sheets in peptides*

Mean parameters of two independent molecules are listed for the oligopeptides except Boc-Val-Pro-Gly-Val-Gly.

		φ	ψ	$C^{\alpha}_{i-1}\cdots C^{\alpha}_{i+1}$	$\angle N-C^{\alpha}-C'$	H-bond lengths
Ala-Ala*-Ala	(*a*)	−151°	148°	7·10 Å	109°	2·98 Å
Boc-Val-Pro-Gly*-Val-Gly	(*b*)	158	−169	7·27	110	3·05
Boc-Val-Pro-Gly-Val*-Gly		−127	132	6·68	108	3·05
Gly-Gly*-Gly	(*c*)	172	174	7·23	110	2·99
Trp-Met*-Asp-Phe-NH_2	(*d*)	−139	161	6·89	108	2·86
Boc-Pro-Met*-Gly-OBzl	(*e*)	−136	138	6·88	110	2·89
β-Poly(Ala)	(*f*)	−139	135	6·95	111	2·77
β-Poly(Val)	(*g*)	−129	123	6·59	106	2·73

References: (*a*) Fawcett, Camerman & Camerman (1975); (*b*) Ayato, Tanaka & Ashida (1981); (*c*) Srikrishnan, Winiewicz & Parthasarathy (1982); (*d*) Cruse, Egert, Viswamitra & Kennard (1982); (*e*) present study; (*f*) Arnott, Dover & Elliott (1967); (*g*) Yamashita & Ashida (1983).

* Parameters for the residues marked with an asterisk are listed.

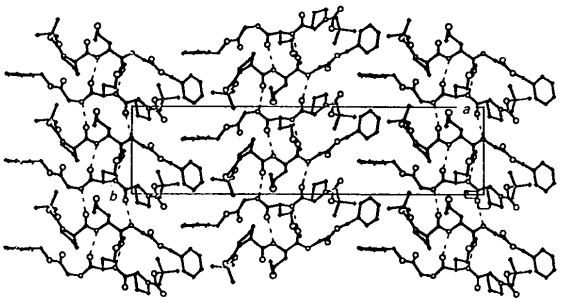

Fig. 3. Crystal structure viewed along the *c* axis, showing ribbons of antiparallel β sheet extended along the *a* axis.

The conformation of the Met side chain was discussed by Stenkamp & Jensen (1975) and Chen & Parthasarathy (1977). Several Met-including peptides have since been studied. The conformation angles listed in Table 3 show clearly the preferred conformations of Met in peptides:

(i) $\chi^1(N-C^{\alpha}-C^{\beta}-C^{\gamma}) = \pm 60°$, *G* or $\bar{G}$,
(ii) $\chi^2(C^{\alpha}-C^{\beta}-C^{\gamma}-S^{\delta}) = 180°$, *T*,
(iii) $\chi^3(C^{\beta}-C^{\gamma}-S^{\delta}-C^{\epsilon}) = 180°$ or $\pm 60°$, mostly *T*, but *G* or $\bar{G}$ are not rare.

The *T* conformation of the bond $N-C^{\alpha}-C^{\beta}-C^{\gamma}$ is found only in Met at the unblocked N-termini and Met monomers (*e.g.* Torii & Iitaka, 1973). Such a difference will probably depend on the difference in the atomic orbitals of N, planar trigonal or steric tetrahedral. In the *T* conformation the $C^{\gamma}-S^{\delta}-C^{\epsilon}$ group moves far away from the bulkier tetrahedral N atom. The $C^{\beta}-C^{\gamma}$ bond is *T* without exception in peptides, only one $\bar{G}$ being found in L-methionine (Torii & Iitaka, 1973). The $C^{\gamma}-S^{\delta}$ bond prefers *T*, but sometimes takes *G* or $\bar{G}$, the conformation being affected mainly by interactions with neighboring side chains.

The packing scheme is shown in Fig. 3. Molecules *A* and *B* are alternately stacked to form a ribbon of an antiparallel β sheet infinitely extended along the *a* axis. A pseudo twofold rotation axis exists at each center of two neighboring peptide molecules which are linked by a pair of hydrogen bonds. All the four hydrogen bonds in the crystal, two each of (Met)N—H···O=C(Met) and (Gly)N—H···O=C(Pro) with the lengths of 2·888 ± 0·026 Å, make up the β sheet.

Several oligopeptides form infinitely extended antiparallel β sheets in the crystals. They are compared in Table 4. A heptapeptide, Met-Glu-His-Phe-Arg-Trp-Gly (Admiraal & Vos, 1983), also has antiparallel β sheets, though details have not been obtained. Such an antiparallel β-sheet formation is clearly one of the most favorable structure patterns for the linear oligopeptide crystals (Ashida, Tanaka & Yamane, 1981; Cruse, Egert, Viswamitra & Kennard, 1982; Admiraal & Vos, 1983). A distinct tendency in pleating of the sheets is shown in Table 4. If the side chain is small, like Gly or Ala, the folding of the chain at the C^{α} atom is small and the chain is more extended, while if the side chain is bulky or especially branched at the C^{β} atom, the chain is more sharply folded at the C^{α} atom to decrease steric repulsions between the side chain and the main chain (Ashida, Tanaka & Yamane, 1981).

Between the molecules there is a rather short C—H···O contact, C(16*B*)—H···O(2*A*) at (−1+*x*,*y*,*z*) with C···O 3·395 (9) Å, H···O 2·43 Å, C(16) being Gly C^{α}. This contact may be a weak hydrogen bond which reinforces the binding of the neighboring molecules in the sheet.

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Structures of 1,4-Bis(3,5-dichloro-2-pyridyloxy)benzene (1), $C_{16}H_8Cl_4N_2O_2$, 1,4-Bis(5-chloro-2-pyridyloxy)benzene (2), $C_{16}H_{10}Cl_2N_2O_2$ and 1,4-Bis(3-chloro-2-pyridyloxy)benzene (3), $C_{16}H_{10}Cl_2N_2O_2$

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Abstract. (1): $M_r = 402{\cdot}1$, triclinic, $P\bar{1}$, $a = 3{\cdot}964$ (1), $b = 7{\cdot}344$ (2), $c = 14{\cdot}546$ (2) Å, $\alpha = 87{\cdot}28$ (2), $\beta = 84{\cdot}97$ (1), $\gamma = 73{\cdot}20$ (2)°, $V = 403{\cdot}7$ (2) Å^3, $Z = 1$, $D_x = 1{\cdot}654$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 6{\cdot}75$ mm^{-1}, $F(000) = 202$, room temperature, $R = 0{\cdot}116$ for 1257 observations. (2): $M_r = 333{\cdot}2$, monoclinic, $P2_1/c$, $a = 3{\cdot}987$ (2), $b = 5{\cdot}587$ (1), $c = 31{\cdot}910$ (2) Å, $\beta = 91{\cdot}20$ (2)°, $V = 710{\cdot}6$ (4) Å^3, $Z = 2$, $D_x = 1{\cdot}557$ Mg m^{-3}, μ(Cu $K\alpha$) = 4·18 mm^{-1}, $F(000) = 340$, room temperature, $R = 0{\cdot}052$ for 1013 observations. (3): $M_r = 333{\cdot}2$, monoclinic, $P2_1/c$, $a = 7{\cdot}367$ (4), $b = 9{\cdot}611$ (1), $c = 21{\cdot}035$ (4) Å, $\beta = 99{\cdot}61$ (2)°, $V = 1468{\cdot}5$ (1·3) Å^3, $Z = 4$, $D_x = 1{\cdot}507$ Mg m^{-3}, μ(Cu $K\alpha$) = 4·05 mm^{-1}, $F(000) = 680$, room temperature, $R = 0{\cdot}078$ for 1919 observations. (1) and (2) induce mouse hepatic monooxygenase activity and are found to have very similar conformations, with the pyridyl rings *anti* (with respect to the phenyl ring), and phenyl–ether dihedral angles of 52·7 (3) and 59·1 (2)°, respectively. In (3), which lacks biological activity, the pyridyl rings are *syn* and the phenyl–ether dihedral angles average 84·0°. In all three compounds the pyridyl rings are nearly coplanar with the C—O—C planes of the ethers and the pyridyl N atoms are proximal to the phenyl ring.

Introduction. The title compounds are members of a series of bis(pyridyloxy)benzene analogs tested for their ability to induce certain monooxygenase enzymes in the liver and proximal intestines of mice (Poland, Mak, Glover, Boatman, Frank & Kende, 1980; Poland, 1982). The majority of these analogs involve variations in the placement and nature of the substituents of the lateral (pyridyl) rings. (1) is the most active compound tested, (2) has significant activity and (3) is inactive. To gain an understanding of the conformational properties of these substances we have performed structure determinations of the title compounds.

Experimental. Experimental parameters are given in Table 1. All data collection: Enraf–Nonius CAD-4 diffractometer; $2\theta_{max} = 154°$; crystals of (1) and (2) grown from chloroform/toluene in sealed dish with a reservoir of ethyl acetate; crystals of (3) grown similarly from chloroform with 2-propanol reservoir; all crystals long, thin needles from which data crystals were cut; Lorentz and polarization corrections applied; empirical (φ curve) absorption corrections applied for (2) and (3); structures solved using *MULTAN*74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974); H atoms located by difference Fourier synthesis; all atoms refined by block-diagonal least squares, using modified counting-statistics weighting scheme; anisotropic temperature factors used for non-H atoms and isotropic temperature factors for H atoms; two low-angle reflections removed from refinement of (2) for

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