(2,2′-$C_8H_6N_4$)-[*closo*-1-Sn-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4$]$_2$ [2·639 (5) Å] (Hosmane, Islam, Siriwardane, Maguire & Campana, 1987). The $B_{(unique)}$—Sn—N bond angles are 95·5 (1), 78·9 (1) and 91·5 (2)°, thus indicating that the Lewis base is not symmetrically bonded to the apical Sn. One of the C_5N planes of the coordinated terpyridine molecule, in particular, the pyridine ring containing N(13), is significantly tilted [13·9 (2)°] from the overall plane of the terpyridine in (II). The mean and the highest deviations of the atoms of the complexed terpyridine from the calculated planes are 0·116 (5) and 0·315 (5) Å, respectively, and are significantly higher than those in the free terpyridine [0·051 (8) and 0·087 (8) Å]. Evidently, the C(115), C(116), N(13) and C(118) atoms of a pyridine ring are responsible for the highest deviation in the Lewis base by their respective values of 0·343 (6), 0·302 (6), −0·233 (4) and −0·252 (6) Å.

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Structure of a Peptide Surrogate, *tert*-Butoxycarbonylalanyl-$\psi(CH_2S)$-phenylalanine [Boc-Ala-$\psi(CH_2S)$-Phe-OH]

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Abstract. $C_{17}H_{25}NO_4S$, $M_r = 339·5$, monoclinic, $C2$, $a = 24·927$ (8), $b = 5·252$ (4), $c = 16·867$ (7) Å, $\beta = 122·70$ (1)°, $V = 1858·2$ (9) Å^3, $Z = 4$, $D_x = 1·21$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1·83$ cm^{-1}, $F(000) = 728$, $T = 295$ K. The final R value for 1466 independent observed reflections is 0·075. The thiomethylene dipeptide analogue possesses a $C_i^\alpha \cdots C_{i+1}^\alpha$ distance somewhat smaller than in the extended amide counterpart due to a partially folded structure, especially in the C-terminal region. Pairs of molecules are held together by O—H···O=C (carboxylic acid) hydrogen bonds.

Introduction. Replacement or modification of peptide backbone functions with D-amino acids, N and α-C substituents, and unnatural amide-bond replacements

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(surrogates) can lead to enzymatically resistant, biologically active analogues. Among the factors contributing to altered chemical and biological parameters are changes in electronic properties, differences in solubility characteristics, resistance to normal proteolytic processes and, perhaps most importantly, conformational changes that can modify receptor recognition (Spatola, 1983). In particular, among a series of isomeric LH-RH analogues containing the $\psi(CH_2S)$ surrogate (IUPAC–IUB Commission on Biochemical Nomenclature, 1984), the activities were highly dependent on the location of the replacement within the peptide backbone (Spatola, Agarwal, Bettag, Yankeelov, Bowers & Vale, 1980): a loss of activity was encountered when an internal amide bond at the site of a critical β-turn was replaced by the more flexible thiomethylene ether moiety, even though activity was often not diminished by substitutions at other positions. More recently, the solution conformation of a cyclic pseudopentapeptide containing a $\psi(CH_2S)$ replacement within the β-turn portion was reported (Spatola, Anwer, Rockwell & Gierasch, 1986). Here we describe the first structural characterization by X-ray diffraction of a $\psi(CH_2S)$ pseudopeptide, namely Boc-Ala-$\psi(CH_2S)$-Phe-OH, a useful intermediate in the synthesis of pseudopeptide hormone analogues.

Experimental. Colourless crystals of Boc-Ala-$\psi(CH_2S)$-Phe-OH were obtained from an ethyl acetate/*n*-hexane solution by slow evaporation. Intensities were collected from a crystal 0·08 × 0·15 × 0·50 mm on a Philips PW 1100 four-circle diffractometer operating in the $\theta/2\theta$ scan mode (with scan width 1·2° and scan speed 0·03° s^{-1}) with graphite-monochromatized Mo $K\alpha$ radiation. Lattice parameters by least-squares refinement of 30 reflections with $10 < 2\theta < 20°$. 1867 reflections up to $\theta = 25°$ were measured, of which 1466 had intensities greater than $2\sigma(I)$ ($-24 \le h \le 25$; $0 \le k \le 7$; $0 \le l \le 20$). During data collection three standard reflections ($\bar{2}21$, $\bar{3}15$, $\bar{2}02$) were measured every 180 min to check the stability of the crystal and the electronics. Intensities were corrected for Lorentz and polarization factors; no absorption correction was applied.

A Patterson synthesis revealed the position of the S atom. The positions of all the other non-H atoms were derived from the subsequent electron density maps. The structure was refined by full-matrix least-squares methods, allowing all the non-H atoms to vibrate anisotropically (with the exception of the phenyl C atoms). The methyl H atoms were refined using the group-refinement procedure, while the methylene, methine and phenyl H atoms were included in calculated positions, but not varied. The H atom of the –COOH group was not located, perhaps because of the statistical disorder present in this group. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = 0{\cdot}87/[\sigma^2(F) + 0{\cdot}01|F|^2]$. Final $R = 0{\cdot}075$ and $wR = 0{\cdot}089$ for 1466 reflections and 306 parameters. In the last cycles of refinement $(\Delta/\sigma)_{max}$ was 0·87 for y of C(4) and $\Delta\rho$ excursions in the final difference map were between –0·27 and 0·43 e $Å^{-3}$.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters (with e.s.d.'s in parentheses) for Boc-Ala-$\psi(CH_2)$-Phe-OH*

$B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}(Å²)
S	0·5283 (1)	–0·5	0·2324 (1)	4·45 (6)
O(1)	0·2686 (2)	–0·2120 (9)	0·1610 (4)	5·0 (2)
O(2)	0·3513 (2)	0·0556 (10)	0·2089 (5)	6·1 (2)
O(3)	0·4671 (2)	–0·071 (1)	0·0734 (3)	5·0 (2)
O(4)	0·5656 (2)	–0·101 (1)	0·1050 (3)	4·9 (2)
N(1)	0·3642 (3)	–0·368 (1)	0·2255 (5)	4·9 (2)
C(1)	0·4453 (3)	–0·489 (1)	0·1957 (5)	4·6 (2)
C(2)	0·4337 (3)	–0·372 (2)	0·2693 (5)	4·9 (2)
C(3)	0·4681 (3)	–0·505 (3)	0·3615 (6)	7·3 (2)
C(4)	0·3297 (3)	–0·155 (1)	0·1985 (5)	4·1 (2)
C(5)	0·2188 (3)	–0·007 (1)	0·1290 (5)	5·2 (2)
C(6)	0·2319 (4)	0·151 (2)	0·2127 (6)	7·0 (2)
C(7)	0·2171 (4)	0·150 (2)	0·0523 (6)	6·6 (2)
C(8)	0·1594 (4)	–0·159 (2)	0·090 (1)	9·4 (2)
C(9)	0·5486 (3)	–0·163 (1)	0·2303 (5)	3·9 (2)
C(10)	0·5281 (3)	–0·106 (1)	0·1315 (4)	3·8 (2)
C(11)	0·6195 (3)	–0·127 (2)	0·2989 (4)	4·1 (2)
C(12)	0·6400 (3)	–0·177 (2)	0·4014 (5)	3·9 (2)
C(13)	0·6794 (4)	–0·379 (2)	0·4500 (5)	4·8 (2)
C(14)	0·6964 (4)	–0·434 (2)	0·5408 (6)	6·1 (2)
C(15)	0·6723 (5)	–0·291 (2)	0·5815 (7)	6·3 (2)
C(16)	0·6334 (4)	–0·088 (2)	0·5364 (6)	6·1 (2)
C(17)	0·6168 (4)	–0·029 (2)	0·4446 (6)	5·6 (2)

Atomic scattering factors and corrections for the real and imaginary parts of the anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed on the IBM 370/158 computer of the University of Padova, using *SHELX*76 (Sheldrick, 1976). Table 1 gives the final atomic coordinates and equivalent isotropic thermal parameters.* The relatively high values of the R factors should be ascribed to the small dimensions of the crystal and the subsequent poor quality of the data.

Discussion. The molecular structure of Boc-Ala-$\psi(CH_2S)$-Phe-OH is illustrated in Fig. 1. Bond lengths and bond angles are listed in Table 2.

The values of the bond lengths and bond angles are in agreement with the literature data on the geometry of Boc urethane derivatives (Benedetti, Pedone, Toniolo, Némethy, Pottle & Scheraga, 1980), amino-acid side chains (Benedetti, Morelli, Némethy & Scheraga, 1983; Gould, Gray, Taylor & Walkinshaw, 1985) and peptide (Benedetti, 1982), carboxylic acid (Dunitz & Strickler,

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44957 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

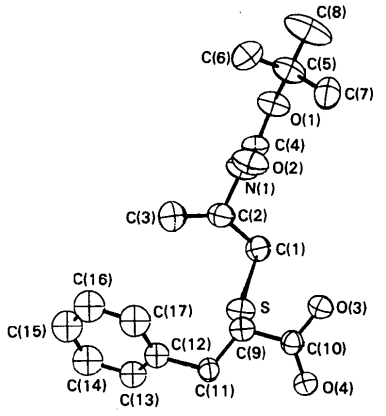

Fig. 1. Molecular structure of Boc-Ala-ψ(CH_2S)-Phe-OH with the numbering of atoms (ellipsoids at 75% probability).

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for Boc-Ala-*ψ(CH_2S)*-Phe*-OH

S–C(1)	1·810 (8)	C(9)–C(10)	1·487 (11)
S–C(9)	1·845 (6)	C(9)–C(11)	1·514 (8)
C(1)–C(2)	1·546 (13)	C(10)–O(3)	1·303 (7)
C(2)–C(3)	1·485 (13)	C(10)–O(4)	1·233 (11)
C(2)–N(1)	1·472 (9)	C(11)–C(12)	1·537 (11)
N(1)–C(4)	1·334 (8)	C(12)–C(13)	1·373 (13)
C(4)–O(2)	1·202 (8)	C(13)–C(14)	1·381 (13)
C(4)–O(1)	1·328 (8)	C(14)–C(15)	1·357 (18)
O(1)–C(5)	1·507 (8)	C(15)–C(16)	1·363 (14)
C(5)–C(6)	1·513 (13)	C(16)–C(17)	1·405 (14)
C(5)–C(7)	1·516 (14)	C(12)–C(17)	1·388 (13)
C(5)–C(8)	1·483 (11)		

C(9)–S–C(1)	103·7 (2)	C(10)–C(9)–C(11)	112·5 (6)
S–C(1)–C(2)	114·3 (5)	S–C(9)–C(11)	109·0 (4)
C(1)–C(2)–C(3)	113·6 (8)	S–C(9)–C(10)	106·5 (4)
C(1)–C(2)–N(1)	106·4 (6)	O(3)–C(10)–C(9)	115·2 (7)
C(2)–N(1)–C(4)	123·4 (7)	O(3)–C(10)–O(4)	121·9 (5)
C(3)–C(2)–N(1)	112·9 (7)	O(4)–C(10)–C(9)	122·8 (7)
N(1)–C(4)–O(2)	124·6 (7)	C(9)–C(11)–C(12)	112·3 (7)
N(1)–C(4)–O(1)	109·6 (6)	C(11)–C(12)–C(13)	120·0 (7)
C(4)–O(1)–C(5)	121·4 (5)	C(11)–C(12)–C(17)	120·9 (8)
O(2)–C(4)–O(1)	125·7 (7)	C(12)–C(17)–C(16)	119·9 (9)
O(1)–C(5)–C(6)	109·6 (6)	C(17)–C(16)–C(15)	118·9 (10)
O(1)–C(5)–C(7)	109·4 (6)	C(16)–C(15)–C(14)	121·8 (9)
O(1)–C(5)–C(8)	102·0 (6)	C(15)–C(14)–C(13)	119·4 (9)
C(7)–C(5)–C(6)	113·0 (7)	C(14)–C(13)–C(12)	121·1 (9)
C(8)–C(5)–C(6)	111·8 (8)	C(13)–C(12)–C(17)	119·0 (8)
C(8)–C(5)–C(7)	110·5 (8)		

1968) and thioether groups (Bigoli, Lanfranchi, Leporati, Nardelli & Pellinghelli, 1982). In particular, those involving the C(1) and S atoms (replacing in this pseudodipeptide analogue the sp^2-hybridized C and N atoms of the peptide moiety) are: (i) the C(2)–C(1), C(1)–S and S–C(9) bond lengths, 1·546 (13), 1·810 (8) and 1·845 (6) Å, respectively, and (ii) the N(1)–C(2)–C(1), C(2)–C(1)–S, C(1)–S–C(9) and S–C(9)–C(10) bond angles, 106·4 (6), 114·3 (5), 103·7 (2) and 106·5 (4)°, respectively.

The phenyl and urethane groups are planar within the experimental uncertainty (r.m.s.d. 0·01 Å). The dihedral angle between the normals to the average plane of the urethane group and those of the phenyl ring system and the carboxylic acid group are 86·1 (3) and 78·2 (6)°, respectively.

With regard to backbone torsion angles, the Boc N-protecting group is in its usual extended (*trans,trans,* or *b*-type) arrangement (Benedetti *et al.,* 1980). The sequence of torsion angles from N(1) to O(3) is −109·7 (8), 177·3 (5), −70·8 (6), −84·2 (5) and 77·2 (7)° (IUPAC–IUB Commission on Biochemical Nomenclature, 1970). The molecule is markedly folded, particularly in its C-terminal region, from C(1) to O(3). Consequently, the C(2)···C(9) separation in this compound is 3·4 (1) Å, somewhat smaller than the $C_i^\alpha \cdots C_{i+1}^\alpha$ separation in an extended peptide chain (3·8 Å) (Ramachandran & Sasisekharan, 1968). The carboxylic acid group adopts an unusual conformation – intermediate between synclinal and anticlinal (Dunitz & Strickler, 1968), the S–C(9)–C(10)–O(4) torsion angle being −100·2 (7)°.

As for the Phe side chain, the χ^1 and χ^2 torsion angles have values of −64·2 (8) and −62·2 (11)°, respectively. The χ^1 value belongs to the most represented class of fully staggered rotameric conformations (g^- conformer) according to recent statistical analyses of side-chain conformations in oligopeptides (Benedetti *et al.,* 1983; Gould *et al.,* 1985). However, a definite preference for the aromatic group of the Phe residue is observed with $\chi^2 \simeq 90°$.

There are no intramolecular hydrogen bonds in Boc-Ala-ψ(CH_2S)-Phe-OH. Rather, pairs of molecules are held together in the crystal state across a crystallographic twofold axis by the formation of two intermolecular hydrogen bonds of the O–H···O=C (carboxylic acid) giving rise to the eight-membered cyclic dimer characteristic of carboxylic acids (Leiserowitz, 1976; Hagler, Dauber & Lifson, 1979) (Fig. 2). The O(3)···O(4)′ ($1-x$, y, $-z$) distance is

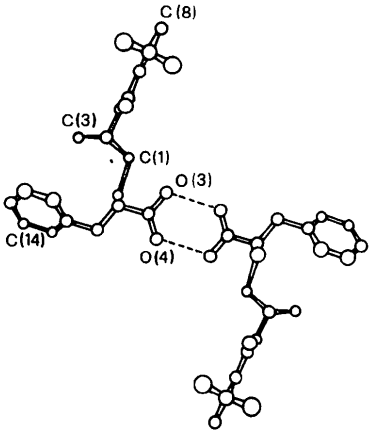

Fig. 2. The cyclic dimer formed by the molecules of Boc-Ala-ψ(CH_2S)-Phe-OH. Intermolecular hydrogen bonds are shown as dashed lines.

2·663 (8) Å, close to the most probable range for an O—H···O hydrogen-bond length (Brown, 1976; Mitra & Ramakrishnan, 1977). The N—H and C=O groups of the urethane moiety are not involved in hydrogen-bond formation. This latter result is at variance with the principle that the maximum number of proton donor and acceptor sites will participate in hydrogen bonds, recently put forward in a study of amides and carboxylic acids (Etter, 1982).

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Structure of 1,3-Bis(carboxymethyl)imidazole

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Abstract. $C_7H_8N_2O_4$, $M_r = 184{\cdot}154$, triclinic, $P\bar{1}$, $a = 7{\cdot}482$ (4), $b = 7{\cdot}698$ (5), $c = 8{\cdot}202$ (3) Å, $\alpha = 107{\cdot}24$ (4), $\beta = 106{\cdot}94$ (4), $\gamma = 106{\cdot}77$ (4)°, $V = 393{\cdot}6$ (3) Å^3, $Z = 2$, $D_m = 1{\cdot}577$ (4), $D_x = 1{\cdot}553$ (3) Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}121$ mm^{-1}, $F(000) = 192$, $T = 296$ K, $R = 0{\cdot}052$ for 2818 unique observed reflections. The molecule is a zwitterion, stabilized by charge delocalization. The imidazole moiety shows a planar arrangement with a maximum deviation of 0·003 (2) Å for C2 and C3. Intermolecular hydrogen bonds of the type O—H···O connect the molecules in an infinite chain along the [111] direction. The chains are joined together by van der Waals forces. The O···O hydrogen-bond length is 2·463 (2) Å.

Introduction. Glyoxal, which occurs in foods as one of numerous degradation products of the main nutrients,

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