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The Conformation of the Cyclic Tetrapeptide L-Ser(O-t-Bu)-β-Ala-Gly-L-β-Asp(OMe) Containing a 14-Membered Ring

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The title compound, $C_{17}H_{28}N_4O_7$, is a synthetic crystalline cyclic tetrapeptide containing alternate α-amino peptide groups and β-amino peptide groups similar to the naturally occurring depsipeptide serratamolide. The tetrapeptide represents a preliminary step in the proposed synthesis of a cylindrical polypeptide. The 14-membered 'ring' consists of four planar segments with each segment in the *trans* conformation. The corner atoms are $C^{\alpha}(1)$, $C^{\beta}(2)$, $C^{\alpha}(3)$ and $C^{\beta}(4)$. Two carbonyl oxygens are directed above the average plane of the ring and the other two below. If the side chains are disregarded, two of the peptide groups are related to the other two by an approximate center of symmetry. In the crystal the molecules are stacked over each other by translation in the **a** direction. Between each pair of molecules in the stack there are two NH···O bonds at 2·86 Å. The remaining two NH moieties do not participate in hydrogen bonding. The space group is $P2_1$ with $a = 5{\cdot}624$ (4), $b = 10{\cdot}298$ (7), $c = 17{\cdot}859$ (13) Å and $\beta = 99{\cdot}07$ (5)°. The structure was solved by the symbolic addition procedure.

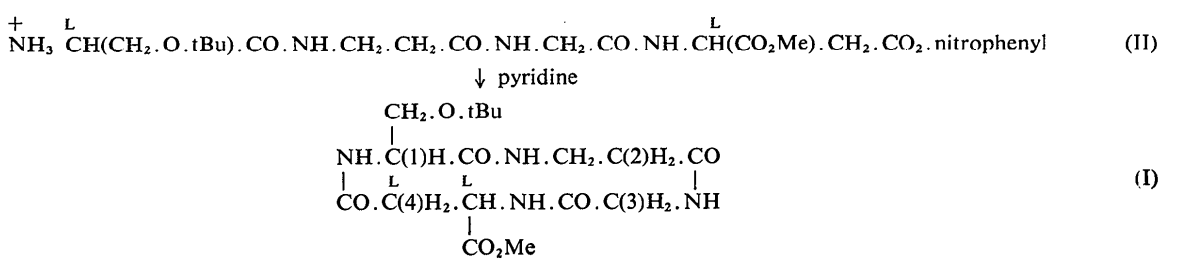
A proposal for the synthesis of cylindrical peptides through the linkage of individual cyclic 14-membered oligotetrapeptides by covalent and hydrogen bonds as shown in Fig. 1 has been put forward in an earlier communication (Hassall, 1972). In order to explore this concept further, the conformation of an individual 14-membered ring peptide, cyclic-L-Ser(O-t-Bu)-β-Ala-Gly-L-β-Asp(OMe), has been determined by a crystal structure analysis. This synthetic peptide is unusual in that it contains two β-amino residues and thus introduces two additional CH_2 groups into the ring; however, the antibiotic serratamolide (Wasserman, Keggi & McKeon, 1961) a natural depsipeptide, has an analogous ring system.

Experimental

The cyclic oligopeptide (I) has been prepared in 55% yield by the cyclization of the linear *p*-nitrophenyl ester (II). Derivative (II) has been synthesized by standard procedures for peptide synthesis and fully characterized. Recrystallization of (I) from methanol produced fine monoclinic needles with the needle axis along the **a** direction.

The crystal data are: space group $P2_1$; $Z=2$; $a=5{\cdot}624$ (4); $b=10{\cdot}298$ (7); $c=17{\cdot}859$ (13) Å and $\beta=99{\cdot}07$ (5)°; $V=1021{\cdot}4$ Å^3; $C_{17}H_{28}N_4O_7$; M.W. 400·44; $D_{calc}=1{\cdot}302$ g cm^{-3}; size $1{\cdot}0\times0{\cdot}12\times0{\cdot}05$ mm; $\mu=8{\cdot}70$ cm^{-1}. Cell parameters and standard deviations were obtained from a least-squares fit to the θ, ω, ψ and φ values of 12 reflections individually centered on a four-circle diffractometer. 1765 data with $2\theta_{max}=126°$ were measured with Cu radiation ($\lambda=1{\cdot}54178$ Å), Ni filter, on an automatic diffractometer with the θ–2θ scan mode, a scan of 2·0° and a scan rate of 2° min^{-1}. The background was counted for 10 s at either end of the scan. Three reflections were monitored at intervals of 50 measurements and their intensities remained constant throughout the data collection. Lorentz and polarization corrections were applied to the data but no absorption correction was made.

Phases were determined directly from the normalized structure factors $|E_{\mathbf{h}}|$ by means of the symbolic addition procedure for space group $P2_1$ (see *e.g.* Karle & Karle, 1968). The origin was specified by assigning a phase value of 0 to reflections 100, 60$\bar{5}$ and 111. Symbols *a*, *b*, *p* and *q* were assigned to reflections 50$\bar{6}$, 1,0,15,



53$\bar{7}$ and 373. The values for a and b are restricted to 0 or π and were determined in the course of the phase determination. The enantiomorph would have to be specified by symbols p or q. If q were assigned a value of $+\pi/2$, then it appeared that $p=-\pi/4$ or $-3\pi/4$. The former value of p yielded an E map which showed most of the atoms in the molecule. Using the phase information from the partial structure in a recycling procedure (Karle, 1968), the remainder of the atoms were located in the following E map. Once the structure was known, a different origin was chosen for a more convenient placement of the molecule in the cell. In addition, all the y coordinates were replaced by $1-y$ so that the absolute configuration of the molecule would correspond to the known chemical configuration. Therefore, the values of the phases associated with the coordinates as presented in Table 1 do not correspond to those chosen for the phase determination.

The function minimized for the least-squares refinement was $\sum w_F(F_o-F_c)^2$ where $w_F=1/\sigma_F^2$. Values for σ_F^2 were obtained in the manner described by Gilardi (1973). Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). A difference map computed after a full-matrix anisotropic refinement on the 28 heavy atoms, $R=9{\cdot}7\%$, contained all the hydrogen atom positions except some of those associated with the terminal CH_3 groups. It was possible to assign reasonable coordinates to the missing hydrogen atoms since the conformations of the CH_3 groups in the t-butyl moiety were fixed by several hydrogen atoms known from the difference map. For C(42), it was assumed that one hydrogen atom was *trans* to the carbonyl carbon and the other two hydrogen atoms straddled the carbonyl oxygen. The calculated coordinates are marked by an asterisk in Table 2. Inclusion of the coordinates for the 28 hydrogen atoms as fixed quantities with $B=5{\cdot}5$ in additional cycles of anisotropic refinement resulted in an R value of 5·7% for all 1765 reflections or an R value of 5·1% for 1691 reflections with $|F|$ values greater than 1σ.*

Results and discussion

Conformation of the molecule

The conformation of the cyclic tetrapeptide is illustrated in the stereodiagram in Fig. 2. Each of the four amide groups of the amino acid residues (both α and β) assumes the *trans* conformation. This result is in contrast to that found for a cyclic tetradepsipeptide containing 12 atoms in the ring in which two peptide groups were in the *cis* conformation (Konnert & Karle, 1969). The two additional CH_2 groups in the ring of the present compound allow the more usual *trans* form. The 14-membered ring contains four nearly planar segments. Each planar segment is approximately perpendicular to the average plane through the ring. The corner atoms are $C^{\alpha}(1)$, $C^{\beta}(2)$, $C^{\alpha}(3)$ and $C^{\beta}(4)$. Carbonyl

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30714 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional coordinates and thermal parameters with standard deviations*

The thermal parameters are of the form $T=\exp[-\frac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)]$. The standard deviations are those calculated by the least-squares program.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	0·5445 (6)	0·7965 (0)	0·8062 (2)	2·95 (15)	2·99 (14)	3·37 (14)	−0·23 (12)	1·09 (11)	−0·42 (13)
$C^{\alpha}(1)$	0·3472 (7)	0·8543 (5)	0·8379 (2)	3·33 (17)	3·20 (18)	3·14 (16)	−0·28 (15)	1·27 (14)	−0·36 (15)
C′(1)	0·1691 (7)	0·9273 (5)	0·7807 (2)	3·29 (19)	2·84 (17)	3·93 (17)	−0·66 (16)	1·17 (15)	−0·57 (15)
O(1)	−0·0359 (5)	0·9490 (4)	0·7949 (2)	2·88 (13)	5·00 (16)	5·61 (15)	−0·19 (13)	1·80 (11)	0·04 (14)
C(11)	0·4480 (8)	0·9473 (5)	0·9016 (2)	4·74 (22)	3·80 (20)	3·62 (17)	0·14 (18)	0·88 (16)	−0·39 (17)
O(11)	0·5828 (6)	0·8738 (4)	0·9596 (2)	5·81 (16)	4·10 (15)	3·62 (12)	0·10 (14)	0·26 (12)	−0·80 (12)
C(12)	0·6931 (8)	0·9415 (6)	1·0262 (2)	3·91 (19)	5·13 (25)	4·00 (19)	−0·22 (19)	0·27 (15)	−1·38 (20)
C(13)	0·8506 (11)	0·8426 (7)	1·0705 (3)	8·65 (37)	6·89 (36)	6·55 (30)	1·79 (32)	−1·60 (29)	−0·83 (28)
C(14)	0·5035 (10)	0·9918 (7)	1·0702 (3)	5·44 (26)	10·60 (43)	4·28 (22)	−0·18 (28)	1·07 (20)	−2·60 (26)
C(15)	0·8403 (10)	1·0579 (7)	1·0063 (3)	4·91 (27)	7·62 (38)	7·68 (31)	−1·45 (27)	0·69 (24)	−1·21 (30)
N(2)	0·2467 (6)	0·9695 (4)	0·7186 (2)	2·96 (15)	3·99 (17)	3·86 (15)	0·28 (13)	1·19 (12)	0·28 (14)
$C^{\beta}(2)$	0·0962 (8)	1·0291 (5)	0·6536 (2)	3·97 (22)	4·20 (22)	4·39 (20)	0·91 (18)	1·10 (17)	0·87 (18)
$C^{\alpha}(2)$	0·0449 (7)	0·9330 (5)	0·5884 (2)	2·53 (17)	4·70 (22)	4·25 (19)	0·21 (17)	1·03 (14)	0·29 (17)
C′(2)	0·2701 (7)	0·8817 (5)	0·5640 (2)	2·50 (18)	4·07 (20)	3·56 (17)	0·08 (16)	0·75 (14)	0·80 (17)
O(2)	0·4719 (5)	0·9280 (4)	0·5873 (2)	2·58 (12)	4·47 (15)	4·66 (14)	−0·55 (12)	0·66 (10)	−0·30 (12)
N(3)	0·2401 (6)	0·7805 (4)	0·5157 (2)	2·96 (15)	4·53 (19)	3·46 (15)	−0·35 (14)	0·98 (12)	−0·36 (15)
$C^{\alpha}(3)$	0·4464 (7)	0·7227 (5)	0·4892 (2)	3·40 (21)	4·88 (24)	3·56 (20)	−0·31 (18)	1·42 (16)	0·05 (17)
C′(3)	0·6144 (8)	0·6500 (5)	0·5482 (2)	3·89 (21)	3·33 (18)	3·19 (16)	−0·64 (17)	1·27 (15)	−0·64 (15)
O(3)	0·8283 (5)	0·6341 (4)	0·5408 (2)	3·03 (13)	4·72 (15)	4·20 (12)	−0·01 (12)	1·76 (11)	0·04 (12)
N(4)	0·5244 (6)	0·6011 (5)	0·6074 (2)	3·76 (17)	4·26 (18)	3·68 (15)	−0·02 (15)	1·52 (13)	0·62 (14)
$C^{\beta}(4)$	0·6735 (8)	0·5399 (5)	0·6706 (2)	4·39 (22)	3·36 (20)	3·81 (19)	0·14 (17)	1·70 (16)	0·14 (17)
$C^{\alpha}(4)$	0·7329 (7)	0·6342 (5)	0·7374 (2)	2·80 (18)	3·56 (20)	4·85 (20)	0·31 (16)	1·06 (15)	−0·55 (17)
C′(4)	0·5114 (7)	0·6880 (5)	0·7631 (2)	3·16 (18)	2·98 (17)	2·87 (15)	−0·34 (15)	1·01 (13)	−0·16 (15)
O(4)	0·3124 (5)	0·6375 (4)	0·7464 (2)	2·80 (12)	4·27 (14)	4·83 (14)	−0·79 (12)	1·18 (11)	−1·38 (12)
C(41)	0·5505 (9)	0·4159 (5)	0·6907 (2)	5·99 (25)	3·12 (20)	3·99 (20)	−0·13 (18)	2·11 (18)	−0·63 (17)
O(41)	0·3703 (7)	0·3704 (5)	0·6558 (2)	6·95 (21)	4·60 (17)	5·22 (16)	−2·07 (17)	1·34 (16)	−0·99 (15)
O(42)	0·6806 (7)	0·3624 (4)	0·7523 (2)	8·03 (21)	3·70 (16)	5·42 (17)	−0·84 (15)	0·89 (15)	1·31 (14)
C(42)	0·6018 (13)	0·2362 (6)	0·7731 (4)	11·84 (44)	3·86 (23)	8·28 (35)	−1·14 (28)	1·66 (31)	2·05 (25)

oxygens O(1) and O(4) are on one side of the average plane of the ring and O(2) and O(3) are on the other side. If the side groups are disregarded, the ring possesses an approximate center of symmetry. The ring in the tetrapeptide has a conformation similar to that proposed for a 14- membered cycloalkane on the basis that the ring be strain-free (Dale, 1966).

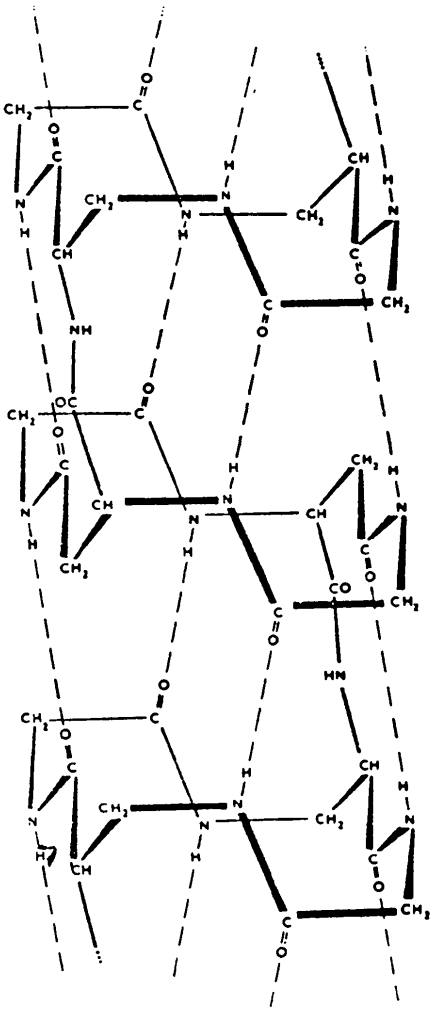


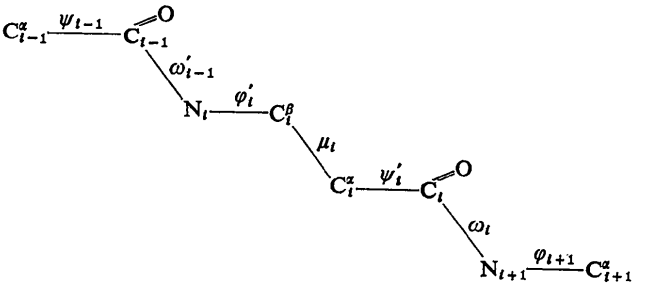
Fig. 1. Projected hydrogen bonding in a proposed cylindrical peptide consisting of 14-membered ring units.

Table 2. *Approximate coordinates for the hydrogen atoms as determined from a difference map*

Assumed coordinates were used for the atoms labelled with an asterisk.

	x	*y*	*z*
H——N(1)	0·717	0·862	0·804
H——C^{α}(1)	0·260	0·784	0·866
H(1)–C(11)	0·310	0·994	0·920
H(2)–C(11)	0·515	1·015	0·880
*H(1)–C(13)	0·736	0·766	1·080
H(2)–C(13)	0·961	0·806	1·037
H(3)–C(13)	0·930	0·875	1·117
*H(1)–C(14)	0·400	1·054	1·040
*H(2)–C(14)	0·414	0·918	1·087
*H(3)–C(14)	0·592	1·038	1·118
*H(1)–C(15)	0·969	1·031	0·976
*H(2)–C(15)	0·731	1·122	0·973
H(3)–C(15)	0·918	1·107	1·053
H——N(2)	0·385	0·936	0·707
*H(1)–C^{α}(2)	0·927	0·873	0·606
H(2)–C^{α}(2)	−0·058	0·977	0·545
H(1)–C^{β}(2)	−0·083	1·051	0·668
H(2)–C^{β}(2)	0·168	1·100	0·631
H——N(3)	0·060	0·733	0·521
H(1)–C^{α}(3)	0·379	0·655	0·449
H(2)–C^{α}(3)	0·530	0·781	0·465
H——N(4)	0·367	0·613	0·599
H(1)–C^{α}(4)	0·860	0·717	0·727
H(2)–C^{α}(4)	0·892	0·599	0·780
H——C^{β}(4)	0·840	0·505	0·647
*H(1)–C(42)	0·420	0·243	0·783
*H(2)–C(42)	0·589	0·172	0·729
*H(3)–C(42)	0·693	0·199	0·818

The accepted nomenclature for conformational angles in peptides (IUPAC-IUB Commission on Biochemical Nomenclature, 1970) has to be modified in order to accommodate β-peptide groups. Accordingly, the following labels are used in the text and in Table 3:



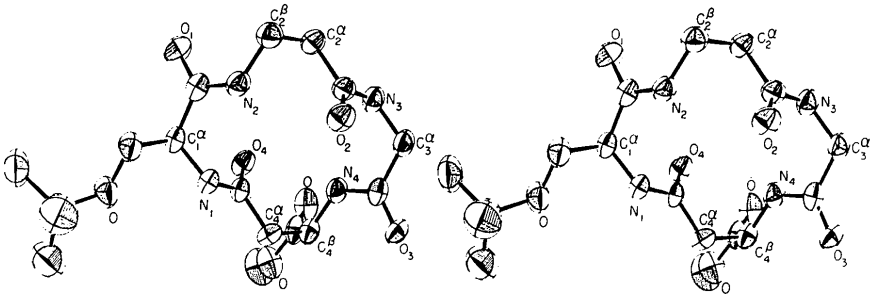


Fig. 2. Stereodiagram of cyclic L-Ser(O-tBu)-β-Ala-Gly-L-β-Asp(OMe).

Although each segment between the corner atoms is nearly planar, the deviations from planarity indicate a convex bowing. The degree of nonplanarity is indicated by the conformational angles ω_i, ω_i' and ψ_i' which would have a value of 180° for planar *trans* conformations. The deviations of individual atoms from the best least-squares plane for each $C^{\alpha}CONC^{\alpha \text{ or } \beta}$ group, listed in Table 4, illustrate the bowing effect. The distances between parallel planes in the peptide ring are 3·2 and 5·0 Å for the two pairs of parallel segments.

Table 3. *Conformational angles**

	L-Ser (O-tBu)	β-Ala	Gly	L-β-Asp (OMe)
i	1	2	3	4
$\varphi_i(\varphi_i')$	−75·2	−103·4	69·3	98·7
$\psi_i(\psi_i')$	−22·8	169·1	25·5	−162·3
$\omega_i(\omega_i')$	173·1	−179·3	−174·3	−176·7
μ_i		−57·6		57·0
χ_i^1	−64·2			6·0
				−176·3
χ_i^2	−179·3			−173·1
χ_i^3	−171·5			
	68·4			
	−51·4			

* The angles are defined in the text.

Table 4. *Least-squares planes and deviations of individual atoms from the planes of the four peptide groups*

The equations for the least-squares plane of each $C^{\alpha}CONC^{\alpha \text{ or } \beta}$ group are:

(1) $1{\cdot}35579\,x + 8{\cdot}99885\,y + 6{\cdot}76770\,z = 13{\cdot}8588$
(2) $0{\cdot}04792\,x + 6{\cdot}52956\,y - 13{\cdot}6605\,z = -1{\cdot}9399$
(3) $0{\cdot}90135\,x + 8{\cdot}91293\,y + 7{\cdot}91829\,z = 10{\cdot}6912$
(4) $-0{\cdot}30355\,x + 5{\cdot}93900\,y - 14{\cdot}2240\,z = -6{\cdot}9291$

where the x, y and z values are the fractional coordinates as listed in Table 1, and the numbers (1)–(4) are the subscript i for the C^{α} atom.

Deviations from least-squares planes in Å

	i=(1)	(2)	(3)	(4)
C_i^{β}		−0·264		+0·393
C_i^{α}	−0·029	−0·004	+0·026	−0·016
C_i'	−0·002	+0·006	−0·003	+0·006
O_i	+0·012	−0·001	−0·010	+0·004
N_{i+1}	+0·063	+0·003	−0·051	+0·027
$C_{i+1}^{\alpha \text{ or } \beta}$	−0·044	−0·003	+0·038	−0·021

Bond lengths and angles are shown in Table 5 for the peptide ring and in Table 6 for the side chains. There are no apparent differences in bond lengths between comparable atoms in the α- and the β-peptide groups. Comparable angles in the α- and β-peptide groups, however, differ by about 2° at N_i, $C_i^{\alpha \text{ or } \beta}$ and C_i'.

Table 5. *Bond lengths and angles in the peptide groups**

	i=1	2	3	4	Average
N_i–C_i^{α}	1·451		1·448		1·449
N_i–C_i^{β}		1·458		1·440	
C_i^{β}–C_i^{α}		1·521		1·534	1·528
C_i^{α}–C_i'	1·514	1·499	1·500	1·500	1·503
C_i'–O_i	1·239	1·241	1·241	1·228	1·237
C_i'–N_{i+1}	1·327	1·346	1·340	1·352	1·341
$C_{i-1}'N_iC_i^{\alpha}$	121·1		120·1		120·6
$C_{i-1}'N_iC_i^{\beta}$		125·2		122·5	123·8
$N_iC_i^{\beta}C_i^{\alpha}$		110·6		111·2	110·9
$C_i^{\beta}C_i^{\alpha}C_i'$		112·7		112·5	112·6
$N_iC_i^{\alpha}C_i'$	113·9		115·1		114·5
$C_i^{\alpha}C_i'N_{i+1}$	117·2	115·6	117·9	115·6	116·6
$C_i^{\alpha}C_i'O_i$	119·3	122·4	120·3	122·6	121·1
$N_{i+1}C_i'O_i$	123·4	121·9	121·9	121·8	122·2

* The e.s.d.'s are 0·006 Å for the individual bond lengths and 0·35° for the bond angles.

Table 6. *Bond lengths* (Å) *and angles* (°) *in the side chains**

$C^{\alpha}(1)$–C(11)	1·525	N(1)C^{α}(1)C(11)	109·4
C(11)–O(11)	1·405	C′(1)C^{α}(1)C(11)	108·7
O(11)–C(12)	1·433	C^{α}(1)C(11)O(11)	107·8
C(12)–C(13)	1·491	C(11)O(11)C(12)	117·6
C(12)–C(14)	1·512	O(11)C(12)C(13)	104·5
C(12)–C(15)	1·530	O(11)C(12)C(14)	110·5
		O(11)C(12)C(15)	111·5
		C(13)C(12)C(14)	111·5
		C(13)C(12)C(15)	111·1
		C(14)C(12)C(15)	107·7
$C^{\beta}(4)$–C(41)	1·522	N(4)C^{β}(4)C(41)	108·8
C(41)–O(41)	1·198	C^{α}(4)C^{β}(4)C(41)	113·5
C(41)–O(42)	1·341	C^{β}(4)C(41)O(41)	125·8
O(42)–C(42)	1·440	C^{β}(4)C(41)O(42)	109·2
		O(41)C(41)O(42)	124·9
		C(41)O(42)C(42)	115·6

* The e.s.d.'s range from 0·006 to 0·009 Å for the bond lengths and from 0·35 to 0·50° for the angles.

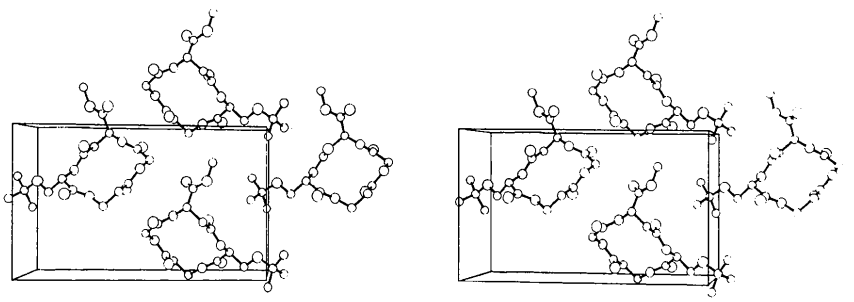


Fig. 3. Stereodiagram of the packing viewed along the *a* axis. The axial directions are *b* ↓ and *c* →.

Packing

The molecular packing in the crystal, viewed down the **a** direction is shown in the stereodiagram in Fig. 3. The tertiary butyl groups from neighboring molecules are interleaved parallel to the **b** direction at the edge of the cell. Near the middle of the cell, with $z \sim \frac{1}{2}$, the carbonyl group in the ester side group and the carbonyl groups with $i=2$ and 3 in adjacent molecules align themselves both in a parallel and antiparallel fashion. The nearest intermolecular approach is between the antiparallel pair C′(2)=O(2), C′(3)=O(3) with O(2)···C′(3)=3·31 Å, C′(2)···C′(3)=3·53 Å and C′(2)···O(3)=3·54 Å. There are no hydrogen bonds between molecules in the **b** and **c** directions.

Intermolecular hydrogen bonding occurs only between molecules stacked by translation along the **a** direction. A stack of three molecules is displayed in the stereodiagram in Fig. 4. Only two hydrogen bonds are formed between each pair of molecules, joining O(1) to HN(1) and O(3) to HN(3) with separations of 2·868 and 2·857 Å, respectively. The O to H distances in these bonds are of the order of 1·7 Å.

This hydrogen-bonding scheme leaves two NH moieties, with $i=2$ and 4, which do not participate in hydrogen bonding. These two nitrogen atoms have several close intra-ring N···O approaches; *i.e.* N(2)···O(2)=2·866 Å with atoms $C^{\beta}(2)$, $C^{\alpha}(2)$ and C′(2) between N(2) and O(2), N(4)···O(4)=2·942 Å with a similar geometry and N(4)···O(41)=2·717 Å. In the latter case, the ester carbonyl is very nearly *cis* to N(4) (the torsional angle χ_4^1 is only 6°); hence O(41) is at nearly a minimum distance to N(4). Even though the N(2)···O(2), N(4)···O(4) and N(4)···O(41) separations are in the range for hydrogen-bond formation, the orientation of the N–H bonds, roughly parallel to the C=O bonds, is not favorable. The O···H separations range from 2·3 to 2·7 Å.

Between each pair of stacked molecules there is a cavity into which the oxygen atoms of the four amide groups protrude. The separations between these oxygen atoms are: O(1)···O(2)′=4·27 Å, O(2)′···O(3)′=3·77 Å, O(3)′···O(4)=4·15 Å, and O(4)···O(1)=3·93 Å (where the primed atoms come from the upper molecule along the *a* axis). The oxygen atoms roughly outline a square which is large enough to accommodate a metal ion like K^+ with K–O ligands of 2·7–2·8 Å. Although the monomer studied here does not appear to form complexes with metal ions, a molecule containing a pair of small cyclic peptides covalently linked by a disulfide bridge does form complexes with K^+ (Schwyzer, Tun-Kyi, Caviezel & Moser, 1970).

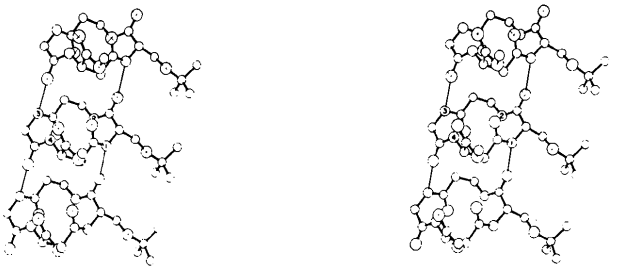
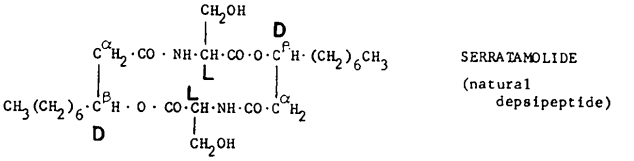


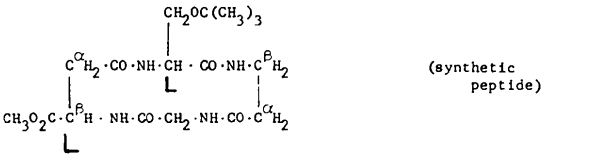
Fig. 4. Stereodiagram of molecules stacked in the **a** direction. The four nitrogen atoms are numbered and the oxygen atoms are designated by X. Two NH···O bonds are formed between each pair of molecules.

Discussion

The conformation of the 14-membered ring peptide in the crystal has many similarities to that postulated in Fig. 1 for the cylindrical peptide. Furthermore in the crystal the individual rings are stacked over each other and the columns are stabilized by hydrogen bonds resembling the scheme postulated in Fig. 1. However, in the crystal of the monomeric unit there are only two hydrogen bonds between pairs of rings instead of four. Moreover, the NH···O bonds are formed between different N and O atoms from those postulated in Fig. 1, *e.g.* N(1)H···O(1) instead of N(1)H···O(4). The average plane of the ring is tilted with respect to the stacking axis by 52° in such a manner that N(1) and O(3) of one molecule are placed over O(1) and N(3) of the adjacent molecule in the column. The difference between the stacking observed in the monomer and the postulated stacking in the polymeric cylindrical peptide may possibly be attributed to the covalent inter-ring bonding in the proposed cylindrical peptide system.

It is interesting to note that the antibiotic serratamolide (Wasserman, Keggi & McKeon, 1961), a natural product, is a tetradepsipeptide that contains a 14-membered ring and has a number of similarities with the molecule under study:





N.m.r. spectra of serratamolide in solution suggest a different conformation with twofold rotation symmetry (Hassall, Moschidis & Thomas, 1971). However, if the conformation of crystalline serratamolide resembled that reported in this study, then the hydrogen-bonding schemes would be compatible in the two substances, since the two NH moieties in the tetrapeptide which do not participate in hydrogen bonding are replaced by O atoms in the serratamolide.

One of the objectives for synthesizing cylindrical peptides is to investigate the possibility of complexa-

tion with metal ions and the transport of these ions across biological membranes. Such a model system designed to simulate various biological functions appears to be feasible. The structural results for the monomer of a cyclic peptide indicate that the proposed conformation for a cylindrical peptide can be largely achieved and that the cavities created by the stacked rings are large enough to accommodate metal ions.

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References

DALE, J. (1966). *Angew. Chem. Int. Ed.* **5**, 1000–1021.
GILARDI, R. D. (1973). *Acta Cryst.* B**29**, 2089–2095.
HASSALL, C. H. (1972). *Chemistry and Biology of Peptides.* Proceedings of the Third American Peptide Symposium, edited by J. MEIENHOFER, Ann Arbor, Michigan, pp. 153–157.
HASSALL, C. H., MOSCHIDIS, M. C. & THOMAS, W. A. (1971). *J. Chem. Soc.* (*B*), pp. 1757–1761.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
IUPAC-IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *Biochemistry*, **9**, 3471–3479.
KARLE, I. L. & KARLE, J. (1968). *Acta Cryst.* B**24**, 81–91.
KARLE, J. (1968). *Acta Cryst.* B**24**, 182–186.
KONNERT, J. & KARLE, I. L. (1969). *J. Amer. Chem. Soc.* **91**, 4888–4892.
SCHWYZER, R., TUNG-KYI, A., CAVIEZEL, M. & MOSER, P. (1970). *Helv. Chim. Acta*, **53**, 15–27.
WASSERMAN, H. H., KEGGI, J. J. & MCKEON, J. E. (1961). *J. Amer. Chem. Soc.* **83**, 4107–4108.

Acta Cryst. (1975). B**31**, 560

The Structures of (Sr,Ba)[(Al,Ga)$_2$(Si,Ge)$_2$O$_8$]. I. The Crystal Structures of the Synthetic Feldspars SrGa$_2$Si$_2$O$_8$ and BaGa$_2$Si$_2$O$_8$

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The crystal structures of the synthetic feldspars SrGa$_2$Si$_2$O$_8$ and BaGa$_2$Si$_2$O$_8$ have been found from X-ray intensities, measured on a diffractometer, and refined by Fourier and least-squares methods. Both structures are similar to that of celsian, with space group *I*2/*c* and 8 formula units per cell. There is complete Ga/Si order in SrGa$_2$Si$_2$O$_8$ ($\langle$Si–O$\rangle$ = 1·614, $\langle$Ga–O$\rangle$ = 1·821 Å) and probably also in BaGa$_2$Si$_2$O$_8$, even though here the mean tetrahedral distances would at first sight suggest some disorder ($\langle$Si–O$\rangle$ = 1·634, $\langle$Ga–O$\rangle$ = 1·805 Å). The divalent cations can be considered seven-coordinated. The deviations of T–O bonds from the expected single-bond values are examined.

Introduction

Compounds of the general formula (Sr, Ba)[(Al, Ga)$_2$(Si, Ge)$_2$O$_8$] are characterized by two principal structure types. The first is monoclinic, body-centred, and has the topology of a feldspar (Megaw, 1974*a*). The second is pseudo-orthorhombic, primitive, and is similar to paracelsian (Smith, 1953; Bakakin & Belov, 1961). The isopolymorphic relationships, and the Al–Ga and Si–Ge substitution in the aluminosilicates of Sr and Ba, are discussed elsewhere (Gazzoni, 1973; Calleri & Gazzoni, in preparation). The present paper describes the structures of the feldspar modification of the Sr and Ba gallosilicates, leaving the paracelsian form of SrGa$_2$Si$_2$O$_8$ to a later paper.

Structure determination

Experimental results

For the X-ray analysis use was made of crystals synthesized by Gazzoni (1973) by crystallization from the melt. The crystal class and space group were determined from Weissenberg and precession photographs: both compounds were assigned to space group *I*2/*c*, assuming the presence of the centre of symmetry at (000) on the analogy with other 14 Å feldspars (*cf.* Newnham & Megaw, 1960). The spots on long-exposure single-crystal photographs of the crystals used for the present investigation did not present any kind of splitting or diffusion.

The unit-cell parameters were refined by a least-