$1/\sigma^2(F_o^2)$]. The final positional parameters are listed for C and O in Table 1 and for H in Table 2.*

Discussion. Fig. 1 shows a perspective view of the molecule. The atomic numbering scheme is given in Fig. 2 which also shows the bond lengths between nonhydrogen atoms of the molecule as well as the corresponding angles. The standard deviations in the distances and angles involving nonhydrogen atoms are in the ranges 0·004–0·007 Å and 0·3–0·4°, respectively.

In addition to the epoxy ring, the molecule consists of four six-membered rings, all in the chair conformation, and of one five-membered ring. The average C—C distance within the five *trans* fused rings is 1·54 Å or close to the normal value for sp^3 hybridized C atoms. The 54 C—H bonds are in the range 0·88–1·18 Å; the mean length is 1·00 Å.

The structure determination establishes the following stereochemistry: peracid epoxidation at the C(18) double bond produces the β-epoxide and hence the isomeric compound obtained by ozone treatment has the α-epoxide structure. The absolute configuration of the molecule was not determined by X-ray crystallographic methods but the chemical evidence available indicates a β-oxygen at C(3).

The present structure may be compared to that of a closely related lupane derivative, 3β-acetoxy-20-hydroxylupane, for which the crystal and molecular structure has been determined from diffractometer data (Watson, Ting & Dominguez, 1972). The conformations of both triterpenes are the same but there seem to be some differences in the bond distances and angles; this is partly due to the epoxy function which brings strain to the *D* and *E* rings. There are differences in other rings which may also be significant. On the other hand, some of the extreme values in both compounds are consistent; for instance the C(8)—C(14) bond length (1·605 Å), which deviates most from the mean in the present structure, is almost the same (1·613 Å) in the 3β-acetoxy-20-hydroxylupane molecule.

In order to study in more detail the molecular structure and the effect of substituents thereon, accurate additional data would be useful; these will soon be available for a related compound 3β-acetoxy-13α,18α-epoxylupane (Hiltunen, 1979).

We thank Dr E. Suokas for suggesting the problem and providing the crystals.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34322 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

Acta Cryst. (1979). B35, 1532–1535

Conformational investigation of *tert*-butoxycarbonylhexa(L-valyl) methyl ester by X-ray techniques.

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Abstract

Observations of extended peptide chains, whose direction is perpendicular to the fiber axis (cross-β structure), have hitherto been confined to fibrous proteins and to some synthetic polydisperse polypeptides of rather low molecular weight. This structure has now been found in some monodisperse linear homo-oligopeptides with aliphatic hydrocarbon side chains. X-ray diffraction photographs of *tert*-butoxycarbonylhexa(L-valyl) methyl ester, $C_{36}H_{66}N_6O_9$, show the characteristic reflections of this form. In addition, the good orientation of suitably prepared specimens has

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enabled a fairly complete determination to be made of the hexapeptide unit cell. *tert*-Butoxycarbonylhexa(L-valyl) methyl ester molecules are packed in a pseudo-orthorhombic lattice with $a = 4{\cdot}80\ (1)$, $b = 50{\cdot}0\ (5)$, and $c = 18{\cdot}60\ (5)$ Å. As regards chain orientation, from the available experimental data, it has not been possible to establish whether the arrangement of the chains within the sheets is parallel or antiparallel.

Introduction

Cyclic and linear oligopeptides have recently been used as model compounds for studies on turns, β-structure and folded segments in protein structure. Furthermore, they can also provide information on end-effects and on the effects of short- and medium-range interactions, allowing more precise conclusions to be drawn concerning the conformations assumed by synthetic polypeptides and proteins.

In recent years, substantial work has been carried out in our laboratory on conformational analysis (Goodman, Naider & Toniolo, 1971; Toniolo & Bonora, 1974, 1975) of a complete series of monodisperse linear homo-oligopeptides derived from valine of general formula t-Boc-(L-Val)$_x$-OMe, where $x = 2{\cdot}7$. By CD, IR and UV techniques, evidence was found that the ordered secondary structure assumed by these low molecular weight peptide molecules is the β-associated one.

The present paper deals with the solid-state conformational features of t-Boc-(L-Val)$_6$-OMe,* obtained by an X-ray investigation.

Experimental

Materials

The synthesis of the monodisperse homo-oligopeptides derived from L-valine has been carried out by Toniolo *et al.* according to procedures already published (Toniolo, 1971). All the peptides are chemically and optically pure.

Methods

Films were prepared by stroking out a drying film until it was solid. Fibers were also drawn by means of claws from a viscous solution of the sample. The solvent used was 2,2,2-trifluoroethanol. Both the films and fibers were then dried *in vacuo* for several hours to remove the solvent. The density was determined by a flotation method in a benzene–carbon tetrachloride mixture, allowing the sample to reach equilibrium position. After one day, the measured density was 1·08 Mg m^{-3}. The films and the fibers were examined in a flat camera with sample to photographic film distance, d, variable from 40 to 100 mm, with Ni-filtered Cu $K\bar{\alpha}$ radiation from a fine- and normal-focus X-ray tube and a 0·6 mm pinhole. Tilted-specimen and equi-inclination techniques were also used. Low-angle reflections were collected on a Rigaku–Denky camera. Molecular models were built from CPK space-filling components (12·5 mm = 1 Å).

Results and discussion

Diffraction pictures showed that high crystallinity is present in the examined compound, which also proved to be sufficiently oriented for a detailed analysis.

The X-ray photograph of t-Boc-(L-Val)$_6$-OMe is presented in Fig. 1. From experimental data, clear evidence was obtained that its structure is of the cross-β type (Geddes,

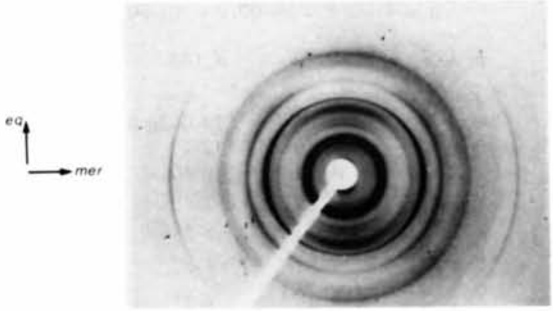

Fig. 1. Normal-beam X-ray diffraction pattern of t-Boc(L-Val)$_6$-OMe oriented film; flat camera, $d = 60$ mm, Cu $K\bar{\alpha}$ radiation; t-Boc(L-Val)$_6$-OMe film and stroking direction horizontal.

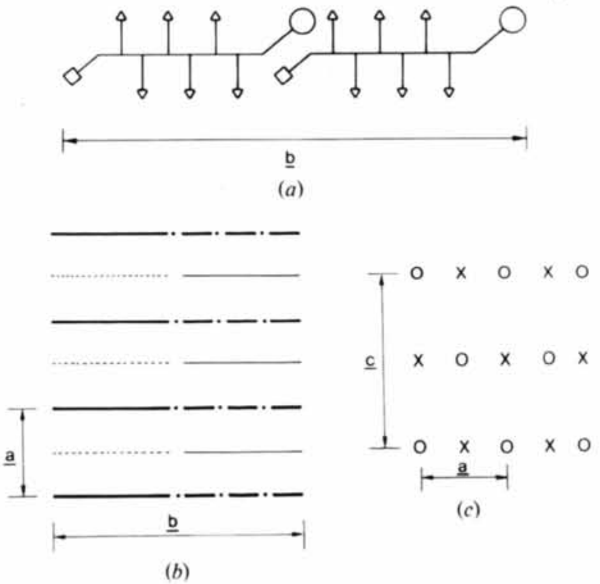

Fig. 2. Schematic representation of the main features of the packing arrangement in the cross-β form of t-Boc(L-Val)$_6$-OMe. The direction of stroking is parallel to a. (a) This diagram brings into evidence the bending of the end groups of two hexapeptide molecules belonging to adjacent sheets. The chain axes of one sheet are displaced by $a/2$ with respect to those of the other. ○, t-Boc; □, OMe; △, isopropyl side chain. (b) Each line represents a hexapeptide chain, while a set of lines of the same kind represents a sheet. The nearest-neighboring sheets, represented by the thick and thin full lines respectively, lie on the ab plane. On the other hand, the sheets represented by the dotted and broken lines lie in a plane parallel to ab, displaced from it by $c/2$. (c) Crosses and circles represent hexapeptide chains projected down b. In the crystal the chains represented by crosses are displaced by $b/2$ with respect to the chains represented by circles.

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* Abbreviations used: t-Boc = *tert*-butoxycarbonyl; OMe = methoxy; L-Val = valine in L configuration.

Parker, Atkins & Beighton, 1968). Specimens prepared as described in the *Experimental* section, mounted with the stroking direction horizontal and normal to the X-ray beam, give diffraction patterns whose main features are a strong arc on the meridian and a strong reflection on the equator. The former reflection, the spacing of which is in the region of 4·6–4·7 Å is related to the distance between hydrogen-bonded peptide chains in a sheet (*a* axis of the unit cell). The latter reflection is related to the distance between consecutive sheets (*c* axis) and its value is 9·3 Å. The *b* axis, which depends on the nearly-extended chain repeat, is perpendicular to the direction of stroking. The peptide chains are relatively so short that their side-to-side aggregation would lead to the formation of a crystallite which is longest in the hydrogen-bond direction, so the oriented fibers contain micelles with their longest dimension parallel to the fiber axis.

Table 1. *t*-Boc-(L-Val)$_6$-OMe *pseudo-orthorhombic cell*: $a = 4{\cdot}80$, $b = 50{\cdot}00$, $c = 18{\cdot}60$ Å

h k l	d_c (Å)	d_o (Å)	I_o*
Equator			
0 2 0	25·00	24·0–26·0	*vs*
0 4 0	12·50	12·47	*mw*
0 4 1	10·38	10·40	*s*
0 0 2	9·30	9·30	*s*
0 5 1	8·81	8·5–8·9	*vs*
0 2 2	8·72		
0 5 2	6·81	6·87	*ms*
0 8 0	6·25	6·21	*m*
0 6 2	6·21		
0 5 3	5·27	5·2–5·5	*vs*
0 8 2	5·19		
0 9 1	5·32		
0 4 3	5·55	4·65	*ms*
0 0 4	4·65		
0 4 4	4·36	4·35	*w*
0 8 3	4·40		
0 10 2	4·40		
0 5 5	3·49	3·46	*w*
0 10 4	3·41		
0 12 3	3·46		
0 11 4	3·25	3·26	*w*
0 13 3	3·26		
0 15 1	3·28		
0 0 6	3·10	3·11	*m*
0 19 0	2·63	2·63	*w*
0 19 1	2·61		
0 18 2	2·66		
0 17 3	2·66		
0 10 6	2·63		
0 21 0	2·38	2·38	*w*
0 21 1	2·36		
0 18 4	2·38		
0 16 5	2·39		
0 24 2	2·03	2·04	*vw*
0 23 3	2·05		
0 22 4	2·04		
First layer line			
1 0 1	4·65	4·65	*vvs*
1 6 2	3·80	3·85	*ms*
1 7 1	3·90		
1 8 0	3·81		
1 0 3	3·80		
1 9 0	3·63	3·61	*w*
1 7 2	3·66		
1 4 3	3·63		
1 3 4	3·28	3·25	*w*
1 8 3	3·24		
1 10 2	3·25		
1 11 1	3·25		
1 0 6	2·60	2·62	*vw*
1 9 5	2·60		
1 12 4	2·61		
1 14 3	2·60		
1 15 2	2·63		
1 16 0	2·62		
Second layer line			
2 0 0	2·40	2·40	*s*
2 5 2	2·26	2·26	*w*
2 7 1	2·26		
2 7 0	2·28		
2 8 0	2·24		
2 0 3	2·24		
2 5 3	2·18	2·19	*vw*
2 8 2	2·18		
2 7 2	2·21		
2 9 1	2·19		
2 9 0	2·20		
2 4 4	2·10	2·09	*vw*
2 5 4	2·09		
2 9 3	2·08		
2 12 0	2·08		
2 12 1	2·07		
2 10 2	2·11		
Third layer line			
3 0 1	1·59	1·60	*m*
3 1 0	1·60		
3 2 0	1·60		
3 1 1	1·59		
3 2 1	1·59		
3 0 0	1·60		

* Abbreviations used: *vvs* = very, very strong; *vs* = very strong; *s* = strong; *ms* = medium strong; *m* = medium; *mw* = medium weak; *w* = weak; *vw* = very weak.

The spacings, d_o, and eye-estimated intensities, I_o, of the observed reflections obtained from a detailed analysis of the X-ray pictures of the hexapeptide, are reported in Table 1. With these data we tried to define the unit-cell dimensions. The equatorial reflection at about 25·0 Å can be directly related to the molecular chain length (*b* axis). Three well-developed layer lines, which appear clearly on the equi-inclination X-ray photographs, indicate that the crystallographic repeat along the meridian is 4·8 Å, *i.e.* twice the spacing of the 200 strong meridional reflection. Finally, the intersheet distance is 9·3 Å as in poly(L-valine) (Komoto, Kim, Ōya & Kawai, 1974) and in the pentamer of the peptide series (Del Pra & Toniolo, 1978).

All observed reflections can be satisfactorily indexed according to a pseudo-orthorhombic unit cell with $a = 4{\cdot}8$, $b = 50{\cdot}0$, and $c = 18{\cdot}6$ Å. The length of the *b* axis is approximately twice the normal molecular chain length indicating that the two chains of the asymmetric unit are different from a crystallographic point of view. The reason for giving the *c* axis the value 18·6 Å instead of 9·3 Å (intersheet spacing) comes from the observation of several reflections with *l* odd, which can only appear if the repeat of the electron density pattern is 18·6 Å (or a multiple of this length). This implies that consecutive hydrogen-bonded sheets appear different as in poly(β-*n*-propyl L-aspartate) (Bradbury *et al.*, 1960) and in poly(*S*-carbobenzoxy-L-cysteine) (Elliott, Fraser, McRae, Stapleton & Suzuki, 1964), where it has been suggested that the side chains are highly ordered and alternate sheets have different side-chain conformations. There are no reflections requiring a to be doubled, but it does not necessarily follow that the parallel-chain type is appropriate. For instance, the molecular model indicates that the length of a single antiparallel chain of a protected hexapeptide with fully-extended end groups is about 3 Å but it is possible to show by means of CPK space-filling components that the closest packing is obtained when: (1) the *t*-Boc and -OMe groups are bent with respect to the backbone direction (Fig. 2*a*) and (2) the chain axes of a sheet are displaced by $a/2$ with respect to the first neighboring sheets (Fig. 2*b*). This lattice, which is in agreement with the experimental data, in particular with the very high intensity of the 101 reflection and with the absence of the 100 reflection, would be favored by the relatively bulky isopropyl side-chain groups too.

The calculated crystal density is $D_c = n \times 0{\cdot}266$ Mg m^{-3}, where n is the number of peptide chains in the pseudo-orthorhombic cell. The comparison with the observed density, $D_o = 1{\cdot}08$ Mg m^{-3}, indicates that such a cell is crossed by four β chains.

We are indebted to Professors C. Toniolo and G. M. Bonora who kindly supplied us with the samples.

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The crystal structure of Li_3ThF_7.

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Abstract

It is pointed out that the unusual coordination polyhedron for the ThF_9 group reported by Cousson, Pagès & Chevalier [*Acta Cryst.* (1978), B**34**, 1776–1778] for Li_3ThF_7, a tetragonal antiprism with a pyramid on one of the square faces, is one of three best arrangements of nine sp^3d^5 bond orbitals found by consideration of the strengths (concentration in the bond directions) of the hybrid bond orbitals. Theoretical considerations and comparison with other structures indicate that the lithium atoms are not in the positions assigned to them in this crystal.

Cousson, Pagès & Chevalier (1978) have reported for the tetragonal crystal Li_3ThF_7 a structure containing ThF_9 groups with the tetragonal antiprism with a cap (a pyramid) on one of the square faces as the coordination polyhedron. They describe this polyhedron as unusual for complex actinide fluorides; the usually occurring polyhedron is the trigonal prism with three lateral caps, as found, for example, in $(NH_4)_3ThF_7$ (Penneman, Ryan & Kressin, 1971) and $RbThF_{13}$ (Brunton, 1971). It is, however, not surprising that both of these coordination polyhedra have been observed, and a third might also be found for these fluorides.

A search for the best set of nine hybrid sp^3d^5 bond orbitals was made by McClure (1970), with the criterion that the sum of the bond strengths (the values of the angular part of the orbital function in the bond directions) be a maximum. The set that he found, the McClure polyhedron, has a mirror plane as its only symmetry element. Two other sets have essentially the same value of the sum of the bond strengths; they are the tetragonal antiprism with one axial cap and the trigonal prism with three lateral caps (Pauling, 1975, 1978). The last of these three has been found in many crystals and molecules and the second in a few, including Li_3ThF_7.

There is little doubt that the reported structure of the ThF_9 group in Li_3ThF_7 is essentially correct, but the positions assigned to the lithium atoms are surely wrong; at least those of two of the three atoms. These two lithium atoms were assigned positions in the same plane as the four F(3) atoms of the complex, at the center of fluorine triangles with a shared edge. They are only 2·03 Å from one another, less than the smallest reported Li···Li distance in any compound: 2·31 Å in Li_2O (2·84 Å in LiF). Moreover, the electrostatic-valence rule (Pauling, 1929) indicates that the axial fluorine atom F(1) and the four F(2) atoms, rather than the two F(3) atoms (which are shared between Th polyhedra), should be involved in most of the bonds to lithium. For ionic valence +4 for Th each of the nine bonds has electrostatic valence $\frac{4}{9}$. Two such bonds nearly saturate the F(3) atoms, whereas each of the F(1) and F(2) atoms