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Crystal Structure of L-Threonyl-L-phenylalanine-*p*-nitrobenzyl Ester Hydrobromide*

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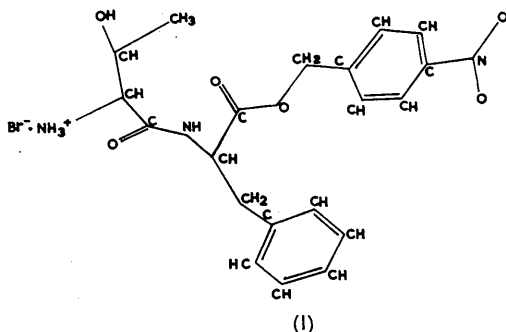
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The crystal structure of L-threonyl-L-phenylalanine-*p*-nitrobenzyl ester hydrobromide, C₂₀N₃O₆H₂₄Br, has been determined using three-dimensional data. The crystals are orthorhombic with space group *P*2₁2₁2₁ and $a = 8.93 \pm 0.02$; $b = 45.75 \pm 0.06$ and $c = 5.05 \pm 0.03$ Å. The final *R* value at the end of three-dimensional refinement is 0.089. A brief discussion of the backbone and side chain conformations is given. All five protons in the structure available for the formation of hydrogen bonds are utilized in forming a three-dimensional network of hydrogen bonds stabilizing the structure.

The X-ray crystallographic investigation of the structure of L-threonyl-L-phenylalanine-*p*-nitrobenzyl ester hydrobromide(I) was undertaken as a part of the project on the determination of the structures of organic compounds of biological importance, being carried out in this laboratory. The material was obtained from Professor S. Akabori, Institute for Protein Research, Osaka, Japan.



Experimental

The crystals, in the form of long thin needles elongated along the *c* axis, were obtained by slow evaporation of an aqueous solution at 45°C. Rotation, Weissenberg and precession photographs were taken with Cu *K*α radiation and the crystal data are given below:

Crystal system:	Orthorhombic
Cell dimensions:	$a = 8.93 \pm 0.02$, $b = 45.75 \pm 0.06$ and $c = 5.05 \pm 0.03$ Å
Space group:	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (<i>h</i> 00, 0 <i>k</i> 0, 00 <i>l</i> absent for <i>h</i> , <i>k</i> or <i>l</i> odd)
Molecular formula:	C ₂₀ N ₃ O ₆ H ₂₄ Br
Number of formula units:	<i>Z</i> = 4
Measured density by flotation:	1.59 g.cm ⁻³
Calculated density:	1.56 g.cm ⁻³ .

A preliminary Weissenberg photograph of the *hk*0 reflexions with Cu *K*α radiation showed that, as a result of the large thermal vibration, the effective range could be covered with Fe *K*α radiation. Further, use of Fe *K*α radiation would make indexing of the spots at high angles relatively easy since with Cu *K*α radiation, the spots tended to coalesce owing to the long *b* axis. Consequently, intensity data were collected with Fe *K*α

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radiation ($\mu=71.0\text{ cm}^{-1}$) using the equi-inclination Weissenberg technique for higher layers for the reflexions hkL , $L=0$ to 3. This was supplemented by the $hk4$ reflexions recorded with $\text{Cu } K\alpha$ radiation ($\mu=32.2\text{ cm}^{-1}$). Thus almost the whole range of the reciprocal lattice accessible to $\text{Fe } K\alpha$ radiation has been sampled. The intensities were measured visually using a calibrated set of intensities recorded from the same specimen and corrected for Lorentz and polarization factors. They were placed on an absolute scale by layerwise Wilson plots (Wilson, 1942). No absorption correction was applied as the crystal used was thin ($t \approx 0.1\text{ mm}$). This specimen was the only one found which was suitable in quality. No data could be collected by mounting the crystal about the a axis because the crystal was brittle.

Structure determination and refinement

A two-dimensional Patterson function using the $hk0$ reflexions gave the x and y coordinates of the bromine atom. A bromine phased Fourier synthesis and a β -synthesis (Ramachandran & Raman, 1959) were computed for this projection. Several attempts to determine the final structure from these maps proved unsuccessful. Subsequently a three-dimensional analysis of the problem was undertaken. The Harker sections at $V=\frac{1}{2}$ and $W=\frac{1}{2}$ were calculated. These gave the x and y coordinates of bromine essentially in agreement with the earlier values deduced from the projection data and indicated that the value of z was near 0.25. It was tentatively put equal to 0.242. One cycle of least-squares refinement using all the 1273 reflexions shifted z to 0.21 leaving x and y practically unchanged. The R -value for bromine alone was 0.404. Using these bromine coordinates a three-dimensional bromine phased electron density map was computed. This map showed the bromine at a height of $52\text{ e.}\text{\AA}^{-3}$ together with 42 other peaks above $2\text{ e.}\text{\AA}^{-3}$. From a study of a spoke model constructed on the basis of the coordinates corresponding to these 42 peaks, it was possible

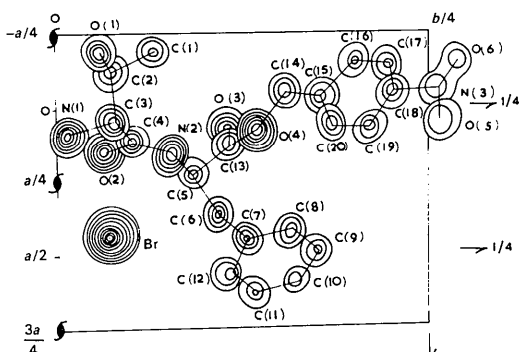


Fig. 1. Perspective view of the electron density distribution along the c axis. Contours are from $2\text{ e.}\text{\AA}^{-3}$ at intervals of $1\text{ e.}\text{\AA}^{-3}$ while near Br, the interval is $5\text{ e.}\text{\AA}^{-3}$. The configuration shown here corresponds to D-threonyl-D-phenylalanine.

to sort out 27 peaks which represented real atomic sites in the crystal. The two remaining atoms, C(7) and C(17), were located at heights of 1.9 and $1.5\text{ e.}\text{\AA}^{-3}$ respectively at the appropriate regions of the map. A structure factor calculation, treating all these 29 atoms as carbons, gave an R value of 0.223.

Four cycles of block diagonal least-squares followed by four cycles of diagonal least-squares refinement minimizing $\sum W(k|F_o| - |F_c|)^2$ with a unit weighting scheme and individual isotropic thermal parameters reduced the R -value to 0.137. The scattering factors were used in the analytical form (Moore, 1963). A three-dimensional difference-Fourier synthesis was computed at this stage. This map showed only small fluctuations in the background level, except for a single peak of height about $1\text{ e.}\text{\AA}^{-3}$ near the bromine. It was therefore concluded that there is no water of crystallization in the structure. Two further cycles of full-matrix least-squares refinement were carried out on a CDC 3600 computer using the program of Gantzel, Sparks & Trueblood (1961). This refinement of the coordinates, individual isotropic vibration parameters and the layer scale factors reduced the R -value to 0.102. A weighting function similar to the one due to Hughes (1941) with $W=1/F_o^2$ if $|F_o| \geq 25$, $=1/25^2$ if $|F_o| < 25$, was employed. The refinement was carried out with 1003 observed reflexions, leaving out 270 unobserved reflexions. The form factors for the various atoms were taken from *International Tables for X-ray Crystallography* (1962).

It has been observed that in polar space groups, the imaginary component of the anomalous dispersion can often produce significant errors in coordinates in the polar directions (Ueki, Zalkin & Templeton, 1966; McDonald & Cruickshank, 1967). Further refinement was therefore carried out with the form factor of bromine corrected for the real and imaginary components (*International Tables for X-ray Crystallography*, Vol. III, 1962). During the collection of the experimental data, attention had not been paid to making sure that they were hkl rather than $hk\bar{l}$ reflexions. This means that the sign of the $\Delta f''$ correction could be positive or negative. Consequently two sets of two cycles of refinement, each with the form factor of bromine corrected for the real component and the $\Delta f''$ correction either positive or negative, were carried out. The R -value at the end of the refinement with the $\Delta f''$ correction positive was 0.092 and with the $\Delta f''$ correction negative was 0.0886. In addition, the negative polarity to the $\Delta f''$ correction gave a lower value of $\sum W(\Delta F)^2$ (11.88 against 12.60). On applying Hamilton's (1965) significance tests it was found that the lowering in R value is in fact significant at the 0.005 level, indicating that the data are $hk\bar{l}$ rather than hkl . Accordingly the z coordinates of the atoms were reversed in sign. On building the model of the molecule based on the revised coordinates, it was found that the configuration corresponded to the correct one for L-threonyl-L-phenylalanine-*p*-nitrobenzyl ester hydro-

bromide. The shifts in the positional parameters in the last cycle of refinement were of the order of $\frac{1}{3}$ th to $\frac{1}{10}$ th of the estimated standard deviation. The positional and isotropic thermal parameters at the end of the refinement are given in Table 1. The values of ob-

served and calculated structure factors are listed in Table 2. A view of the three-dimensional electron density distribution along the *c* axis is shown in Fig. 1.

Discussion of the structure

(a) Intermolecular packing

The crystal structure is stabilized by a three-dimensional network of hydrogen bonds. There are five protons in the molecule which can take part in hydrogen bonding and all of them are involved in intermolecular hydrogen bonds. There are five near neighbours to the nitrogen atom N(1): Br(II), Br(III), Br, O(2)(II) and O(2)(I) at distances of 3.42, 3.26, 3.39, 2.94 and 2.88 Å respectively. The angles at the nitrogen, namely C(3)-N...X (acceptor) are 135°, 112°, 88°, 150° and 86°. On the basis of these values it is seen that N(1)...O(2)(II) seems to be a normal ionic contact rather than a hydrogen bond. In order to find out the nature of the N(1)...O(2)(I) contact the positions of the hydrogen atoms of the NH₃⁺ group were fixed from geometrical considerations using (i) the bond length N-H = 1.0 Å; (ii) the tetrahedral distribution of hydrogens at the nitrogen atom and (iii) the staggered disposition of the N-H bonds. The hydrogen nearest to O(2)(I) was as distant as 2.55 Å and, further, the hydrogen was far from the line of N(1)...O(2)(I), the angle N(1)-H...O(2)(I) being 98.8°. It is therefore concluded that the N(1)...O(2)(I) is also a normal ionic contact. Here we have an example of five negatively charged atoms approaching a protonated amino group within hydrogen bond distances, while only three of them are hydrogen bonded. A similar situation

Table 1. Atomic coordinates

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Br	0.4563	0.0363	-0.2124	3.8
O(1)	-0.1867	0.0274	-0.2971	6.6
O(2)	0.1609	0.0342	0.2928	4.2
O(3)	0.0867	0.1138	0.6459	5.2
O(4)	0.0810	0.1334	0.2491	4.9
O(5)	0.0577	0.2573	-0.4391	8.8
O(6)	-0.1391	0.2700	-0.2244	11.2
N(1)	0.1013	0.0101	-0.1919	3.6
N(2)	0.1678	0.0786	0.0954	2.9
N(3)	-0.0322	0.2556	-0.2774	9.7
C(1)	-0.1804	0.0644	0.0434	5.8
C(2)	-0.1215	0.0366	-0.0524	5.4
C(3)	0.0496	0.0401	-0.1194	3.4
C(4)	0.1372	0.0513	0.1133	3.9
C(5)	0.2473	0.0936	0.3023	4.0
C(6)	0.3790	0.1102	0.1995	4.6
C(7)	0.4615	0.1282	0.4043	5.2
C(8)	0.4231	0.1556	0.4390	5.6
C(9)	0.4963	0.1717	0.6179	5.8
C(10)	0.6042	0.1604	0.7738	7.4
C(11)	0.6392	0.1319	0.7450	6.1
C(12)	0.5707	0.1146	0.5449	5.4
C(13)	0.1351	0.1139	0.4216	3.7
C(14)	-0.0452	0.1517	0.3348	5.8
C(15)	-0.0247	0.1782	0.1695	4.4
C(16)	-0.1388	0.1985	0.2231	5.7
C(17)	-0.1367	0.2244	0.0698	6.3
C(18)	-0.0311	0.2272	-0.1269	6.0
C(19)	0.0799	0.2084	-0.1728	5.6
C(20)	0.0739	0.1827	-0.0250	4.8

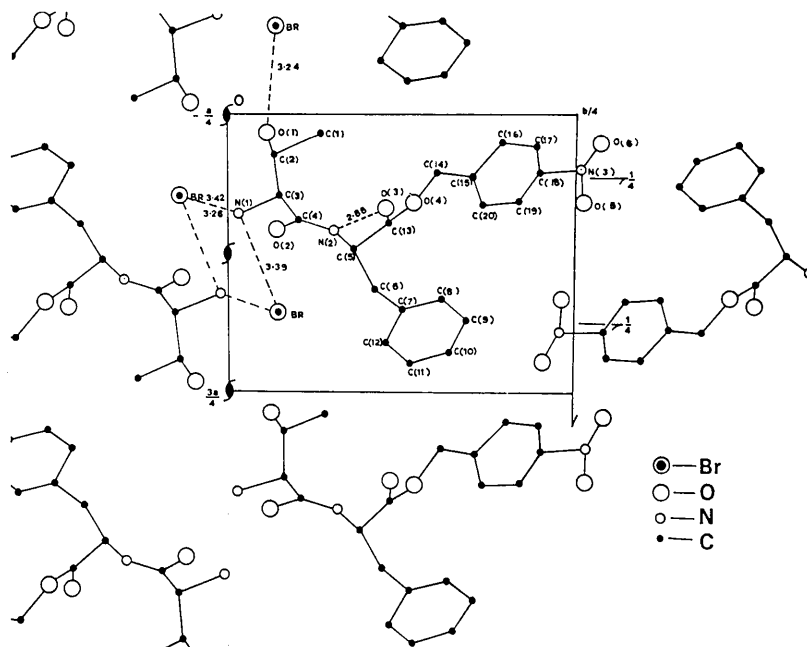


Fig. 2. The view of the structure projected down the *c* axis.

has been found to occur in many other structures found in the literature, for example in L-valine hydrochloride (Ando, Ashida, Sasada & Kakudo, 1967), and in L-leucine hydrobromide (Subramanian, 1967). The atom O(1) of the threonyl side group is at a distance of 3.24 Å from Br(VI) and the angle C(2)–O(1)···Br(VI) is 104°. This seems to be a hydrogen bond of average strength. The atom O(3) of the molecule translated one unit along the *c* axis is in the right direction to form an N(2)–H···O(3)(I) bond of length 2.88 Å. The angle C(4)–N(2)···O(3)(I) is 123°. A view of the structure projected down the *c* axis is shown in Fig. 2. The hydrogen bond distances and angles are given in Table 3. The intermolecular non-bonded contacts less than 3.6 Å are listed in Table 4. It is seen that there is a contact of 3.14 Å between atoms C(3) and O(2)(I) which is rather short, but larger than even the normal limits for this contact of Ramachandran, Ramakrishnan & Sasisekharan (1963). There is one hydrogen attached to the atom C(3) and this can be fixed from geometric considerations. The angle H–C(3)···O(2)(I) comes out to be 59° and it would thus appear that this should be regarded as just an ordinary contact rather than a C–H···O bond. Table 5 presents intramolecular non-bonded distances between third neighbours in the molecule.

Table 3. *Hydrogen bond distances and angles*

Crystal-chemical unit	Symmetry code			Distance d_{ij}
	<i>x</i>	<i>y</i>	<i>z</i>	
I	<i>x</i>	<i>y</i>	<i>z</i> – 1	
II	$\frac{1}{2} - x$	– <i>y</i>	$z - \frac{1}{2}$	
III	$\frac{1}{2} - x$	– <i>y</i>	$\frac{1}{2} + z$	
IV	$x - \frac{1}{2}$	$\frac{1}{2} - y$	–1 – <i>z</i>	
V	$\frac{1}{2} + x$	$\frac{1}{2} - y$	– <i>z</i>	
VI	<i>x</i> – 1	<i>y</i>	<i>z</i>	
N(1)–H···Br(II)	3.42 Å	C(3)–N(1)···Br(II)	135°	
N(1)–H···Br(III)	3.26	C(3)–N(1)···Br(III)	112	
N(1)–H···Br	3.39	C(3)–N(1)···Br	88	
O(1)–H···Br(VI)	3.24	C(2)–O(1)···Br(VI)	104	
N(2)–H···O(3)(I)	2.88	C(4)–N(2)···O(3)(I)	123	

Table 4. *Intermolecular non-bonded contacts less than 3.6 Å*

Atom <i>i</i>	Atom <i>j</i>	Distance d_{ij}
C(3)	O(2)(I)	3.14 Å
O(4)	O(3)(I)	3.18
C(3)	O(3)(I)	3.59
C(20)	O(3)(I)	3.57
C(6)	C(11)(I)	3.41
O(5)	C(17)(I)	3.38
O(2)	Br(III)	3.39
O(6)	O(5)(IV)	3.43
C(9)	O(5)(V)	3.42
O(5)	C(17)(V)	3.41
O(5)	C(16)(V)	3.56
C(9)	O(6)(V)	3.54
C(20)	O(6)(V)	3.58
C(19)	O(6)(V)	3.36

Table 5. *Intramolecular non-bonded distances between third neighbours in the molecule*

Atom <i>i</i>	Atom <i>j</i>	Distance d_{ij}
O(1)	N(1)	2.74 Å
O(2)	N(1)	2.74
O(2)	C(2)	3.07
O(2)	C(5)	2.83
O(3)	N(2)	3.29
O(3)	C(6)	3.45
O(3)	C(14)	2.62
O(4)	C(6)	2.87
O(4)	N(2)	2.73
O(4)	C(20)	2.65
O(4)	C(16)	3.57
O(6)	C(19)	2.62
O(6)	C(17)	3.45
O(5)	C(19)	3.44
O(5)	C(17)	2.56
N(1)	N(2)	3.50
N(2)	C(2)	3.31
C(1)	C(4)	2.92
C(4)	C(6)	3.48
C(4)	C(13)	3.26
C(5)	C(8)	3.32
C(5)	C(12)	3.28
C(7)	C(13)	2.99
C(13)	C(15)	3.51

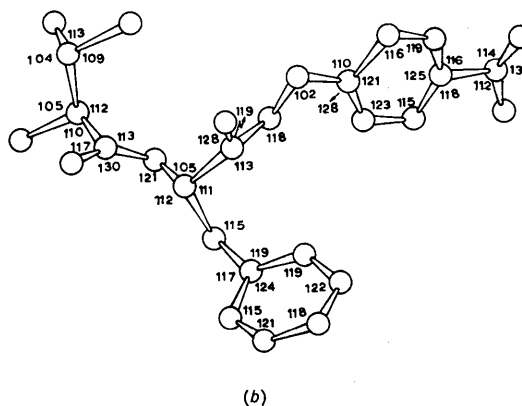
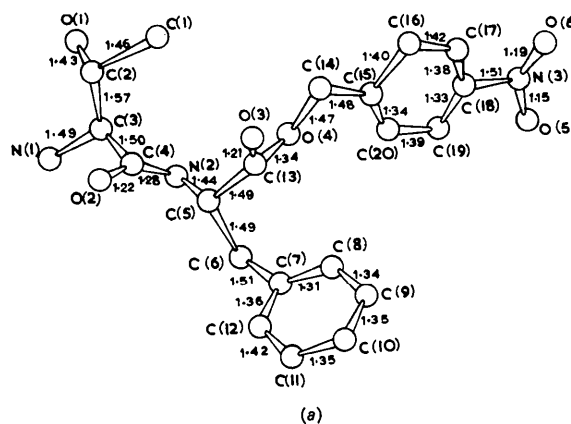


Fig. 3. Bond lengths and bond angles observed in the molecule.

It is worth mentioning that, as might be expected, most of the atoms of the phenyl and nitrobenzyl groups have a larger thermal vibration than those in the remaining part of the molecule which are involved in the hydrogen bonding network.

(b) *Bond distances and angles*

The bond distances and angles calculated from the parameters in Table 1 are shown in Fig. 3 and listed in Table 6. The equations for the best planes of the peptide group, of the two benzene rings and of the group of atoms C(18), N(3), O(5) and O(6) are given in Table 7, together with the deviations of the individual atoms from these planes. None of these deviations is significant.

In view of the relatively large standard deviations in the atomic parameters it is perhaps not fruitful to undertake a detailed discussion of the individual bond distances and angles. In general these values are in agreement with those found in the literature for similar compounds. The average C-C distances are 1.36 Å and 1.39 Å within the two benzene rings of the phenylalanine and nitrobenzyl part of the molecule. The dimensions of the nitro group comprising atoms N(3), O(5) and O(6) are close to the values found for other nitro compounds. The nitro group is coplanar with the benzene ring within the experimental error. The distances within the peptide group consisting of atoms C(3), C(4), O(2), N(2), and C(5) agree with the standard values of Pauling & Corey (1953). The C(3)-N(1) [(C^α-N)] distance of 1.49 Å is close to the average value of 1.487 Å for this distance in amino acids and peptides (Marsh & Donohue, 1967).

The bond lengths and bond angles in the threonyl part of the molecule show a similar trend to that ob-

Table 6. *Intramolecular bond lengths and bond angles*

Bond	Distance	Bond	Distance
C(1)-C(2)	1.46 Å	C(5)-C(13)	1.49 Å
O(1)-C(2)	1.43	C(13)-O(3)	1.21
C(2)-C(3)	1.57	C(13)-O(4)	1.34
C(3)-N(1)	1.49	O(4)-C(14)	1.47
C(3)-C(4)	1.50	C(14)-C(15)	1.48
C(4)-O(2)	1.22	C(15)-C(16)	1.40
C(4)-N(2)	1.28	C(16)-C(17)	1.42
N(2)-C(5)	1.44	C(17)-C(18)	1.38
C(5)-C(6)	1.49	C(18)-C(19)	1.33
C(6)-C(7)	1.51	C(19)-C(20)	1.39
C(7)-C(8)	1.31	C(20)-C(15)	1.34
C(8)-C(9)	1.34	C(18)-N(3)	1.51
C(9)-C(10)	1.35	N(3)-O(5)	1.15
C(10)-C(11)	1.35	N(3)-O(6)	1.19
C(11)-C(12)	1.42		
C(12)-C(7)	1.36		

Bond	Angle	Bond	Angle
O(1)-C(2)-C(1)	113°	C(5)-C(13)-O(3)	128°
O(1)-C(2)-C(3)	104	C(5)-C(13)-O(4)	113
C(1)-C(2)-C(3)	109	O(3)-C(13)-O(4)	119
C(2)-C(3)-C(4)	112	C(13)-O(4)-C(14)	118
C(2)-C(3)-N(1)	105	O(4)-C(14)-C(15)	102
N(1)-C(3)-C(4)	110	C(14)-C(15)-C(16)	110
C(3)-C(4)-O(2)	117	C(14)-C(15)-C(20)	128
C(3)-C(4)-N(2)	113	C(20)-C(15)-C(16)	121
O(2)-C(4)-N(2)	130	C(15)-C(16)-C(17)	116
C(4)-N(2)-C(15)	121	C(16)-C(17)-C(18)	119
N(2)-C(5)-C(6)	112	C(17)-C(18)-C(19)	125
N(2)-C(5)-C(13)	105	C(17)-C(18)-N(3)	116
C(6)-C(5)-C(13)	111	C(19)-C(18)-N(3)	118
C(5)-C(6)-C(7)	115	C(18)-C(19)-C(20)	115
C(6)-C(7)-C(8)	119	C(19)-C(20)-C(15)	123
C(6)-C(7)-C(12)	117	C(18)-N(3)-O(6)	114
C(12)-C(7)-C(8)	124	C(18)-N(3)-O(5)	112
C(7)-C(8)-C(9)	119	O(5)-N(3)-O(6)	133
C(8)-C(9)-C(10)	122		
C(9)-C(10)-C(11)	118		
C(10)-C(11)-C(12)	121		
C(11)-C(12)-C(7)	115		

Table 7. *Best planes through various groups of atoms*

The equations of the planes are expressed in the form $AX+BY+CZ=D$ where X, Y, Z refer to atomic coordinates in Å and D is the origin-to-plane distance.

Plane	Atom	Deviation	A	B	C	D
Peptide group	C(3)	-0.014 Å	0.865	-0.236	-0.442	0.230
	C(4)	0.022				
	O(2)	-0.010				
	N(2)	0.004				
	C(5)	-0.006				
Benzene ring of the phenylalanine part of the molecule	C(7)	-0.002	0.687	0.268	-0.675	3.029
	C(8)	-0.020				
	C(9)	0.017				
	C(10)	0.010				
	C(11)	-0.027				
	C(12)	0.023				
	C(15)	0.011	0.599	0.444	0.667	4.047
Benzene ring of the nitrobenzyl part of the molecule	C(16)	-0.006				
	C(17)	0.015				
	C(18)	-0.026				
	C(19)	0.031				
	C(20)	-0.025				
	C(18)	-0.015	0.571	0.453	0.685	4.131
	N(3)	0.048				
Group of atoms C(18), N(3), O(5) and O(6)	O(5)	-0.018				
	O(6)	-0.015				

served in L_s-threonine (Shoemaker, Donohue, Schoemaker & Corey, 1951), as shown in Fig. 4.

The C(1)–C(2) bond is considerably shorter in these two cases (1.46 and 1.50 Å). In addition the bond angles C(3)–C(2)–O(1) and C(3)–C(2)–C(1) show marked deviation from the tetrahedral value. It should be mentioned, however, that the deviation of the angle C(3)–C(2)–C(1), in the present investigation is within the 2σ level [$\sigma(\theta) = 2^\circ$]. Another noticeable feature is the short length (1.33 Å) of the bond C(13)–O(4), which suggests an appreciable double bond character for this bond. The deviation of C(14) from the best plane through the atoms C(5), C(13), O(3) and O(4) is 0.18 Å, which is statistically significant. Since the atom C(14) is occupying a position *cis* with respect to C(13)–O(3), steric hindrance between O(3) and C(14) perhaps necessitates the out of plane positioning of C(14).

(c) Conformation of the molecule

The backbone conformation of a peptide could be described by the angles φ , ψ – the angles of rotation about the N–C α and C α –C' bonds of the peptide plane (Ramachandran, 1962; Sasisekharan, 1962). The notation and convention followed here is that of Edsall, Flory, Kendrew, Liquori, Nemethy, Ramachandran & Scheraga (1966). In this case, we have one angle φ and one angle ψ for the N-terminal threonyl residue and two angles ψ_1 and ψ_2 for the C-terminal phenylalanyl residue. These angles are 70°, 318°, 119° and 301° respectively and are shown in Fig. 5. It may be mentioned that the values for these angles lie within the allowed regions of the φ - ψ diagram of Ramachandran and his co-workers for peptide configurations redrawn in the new notation of the recent paper by Edsall *et al.* (1966).

The values for ψ_1 and ψ_2 at the C-terminal of a peptide are in general found to be close to 180° and 360° with the exception of glycyl-L-asparagine (Pasternak, Katz & Corey, 1954). In the case of glycyl-L-asparagine the values are $\psi_1 = 249.2^\circ$ and $\psi_2 = 63.3^\circ$ (Lakshminarayana, Sasisekharan & Ramachandran, 1967). The deviation in the present investigation also is large but in the opposite direction, being about -60° . It is interesting to note that in both cases the C-terminal group is not a carboxyl one but an amide or an ester group. The deviation of ψ_1 and ψ_2 in the present case of L-threonyl-L-phenylalanine-*p*-nitrobenzyl ester hydrobromide may be attributed to the formation of a hydrogen bond between the peptide nitrogen and the carboxyl oxygen O(3) of the molecule translated along the shortest axis (*c* axis). A further consequence of this hydrogen bond formation is that the N(2)⋯O(4) distance of 2.73 Å (Table 5) is rather short.

The side chain conformations are described by the torsion angles around the bonds C α –C β , C β –C γ . These angles are close to 60°, 180° and 300° respectively corresponding to the three staggered positions around the bonds and the C γ or C δ atom is said to go into posi-

tions I, II and III respectively (Ramachandran & Lakshminarayana, 1966). In the present case the C γ atom [C(1)] of the threonyl side chain goes into position II and the hydroxyl oxygen O(1) into position III. In fact $\chi^{11} = 298^\circ$ and $\psi^{12} = 176^\circ$. The C γ atom C(7) of the phenylalanine side chain goes into position II with $\chi^1 = 171^\circ$. The views of the side chains looking along the respective C α –C β bonds are given in Fig. 6. The side group conformation of the threonine molecule in the crystal structure of L_s-threonine (Shoemaker *et al.*, 1951) is the same as the one found here with $\chi^{11} = 305^\circ$. In the structure of glycylphenylalanylglycine (Marsh & Glusker, 1961) the C γ atom goes into position II

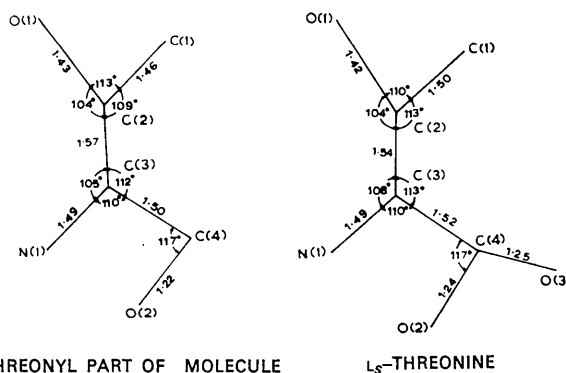


Fig. 4. Bond lengths and bond angles in (a) the threonyl part of the molecule and (b) the L_s-threonine.

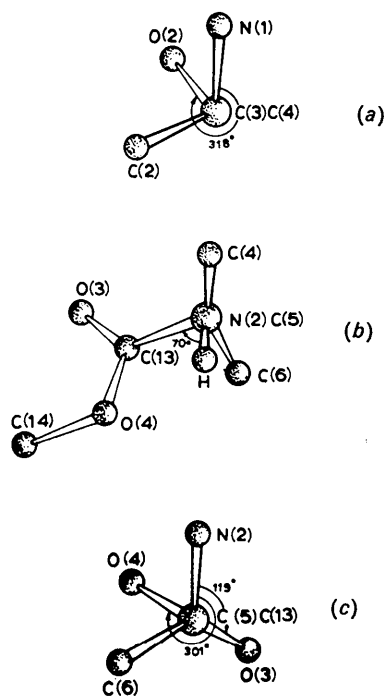


Fig. 5. Backbone conformation: (a) the angle ψ for the N-terminal threonyl group, (b) the angle φ , and (c) the angles ψ_1 and ψ_2 for the C-terminal phenylalanine group.

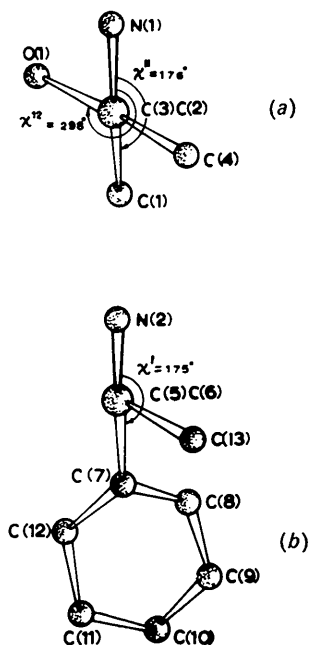


Fig. 6. Side chain conformation: (a) the angles χ^1 and χ^2 for the threonyl group and (b) the angle χ^1 for phenylalanine.

($\chi^1 = 185^\circ$) and in L-phenylalanine hydrochloride (Gurskaya, 1964) it goes into position I ($\chi^1 = 62^\circ$).

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The Crystal Structure of $\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$

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$\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$ crystallizes in the orthorhombic system. The space group is $P2_12_12_1$; the unit-cell parameters are: $a = 6.71$, $b = 9.00$, $c = 7.40$ Å and $Z = 4$. The three positional coordinates together with an isotropic temperature factor for each atom were refined by a three-dimensional least-squares method using 556 reflexions, the final R value being 0.114. The positions of the hydrogen atoms were not determined. The crystal structure is formed by chains consisting of deformed octahedra $\text{Cu}[\text{O}_3(\text{H}_2\text{O})_3]$, which are connected at the vertices. The chains extend parallel to \mathbf{b} and are mutually bonded by PO_3 groups. The structure is closely related to that of $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{CuTeO}_3 \cdot 2\text{H}_2\text{O}$.

Introduction

The crystal structure of $\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$ was determined as a part of a general study of the structure and

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properties of phosphites. The specimen examined was prepared by Nessler (1964).

The aim of the structure analysis of $\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$ was to elucidate the role of the phosphite group HPO_3^{2-}