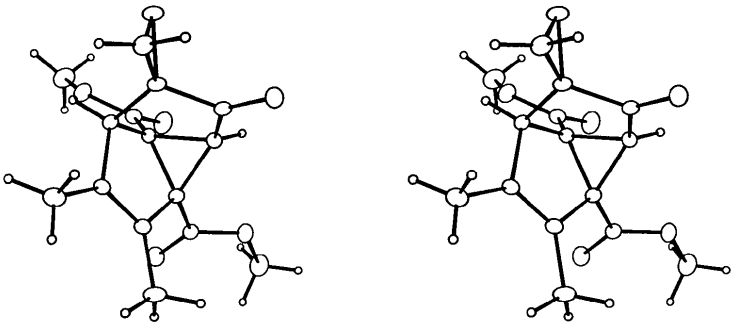

Fig. 2. Stereoview of the molecule.

Table 4. *Torsion angles in the rings* (°)

C(1)–C(2)–C(3)–C(4)	0·6	C(1)–C(5)–C(6)–C(7)	14·9
C(2)–C(3)–C(4)–C(5)	18·8	C(5)–C(6)–C(7)–C(8)	−5·1
C(3)–C(4)–C(5)–C(1)	−29·9	C(6)–C(7)–C(8)–C(1)	−7·2
C(4)–C(5)–C(1)–C(2)	30·1	C(7)–C(8)–C(1)–C(5)	15·8
C(5)–C(1)–C(2)–C(3)	−19·3	C(8)–C(1)–C(5)–C(6)	−18·3

dienones (Becker & Ruge, 1975). These authors used chemical and NMR methods to propose the structure of the products and, as a confirmation of this, a crystal structure investigation has been undertaken. The proposed structure proved to be correct.

A drawing of the content of the asymmetric unit, giving the atomic numbering scheme, is shown in Fig. 1. Intramolecular bond distances and angles are listed in Tables 2 and 3. Stereodiagrams of the structure (Johnson, 1965) are given in Figs. 2 and 3.* Table 4 shows the torsion angles of the two five-membered rings. The three-membered ring, C(4)–C(13)–O(6), is approximately normal (88·5°) to the connecting five-membered ring, the latter being defined by C(1) to C(5).

The author thanks Dr H.-D. Becker for supplying the crystals and suggesting the problem, and Dr John Wood for revising the English text. This work has been supported by the Swedish Natural Science Research Council (Contract No. 2318).

* Fig. 3 has been deposited. See preceding footnote.

References

BECKER, H.-D. & RUGE, B. (1975). *Angew. Chem.* **82**, 782–783.

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1974). *MULTAN* 74, *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. York, England, and Louvain, Belgium.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1978). B**34**, 2640–2643

tert-Butyloxycarbonyl-L-prolylsarcosine

BY H. ITOH, T. YAMANE AND T. ASHIDA

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464, *Japan*

(*Received* 13 *February* 1978; *accepted* 3 *April* 1978)

Abstract. $C_{13}H_{22}N_2O_5$, $M_r = 286{\cdot}33$, orthorhombic, $P2_12_12_1$, $a = 13{\cdot}955$ (1), $b = 16{\cdot}767$ (1), $c = 6{\cdot}662$ (1) Å, $Z = 4$, $D_m = 1{\cdot}22$, $D_x = 1{\cdot}218$ g cm^{-3}, μ(Cu $K\alpha$) = 7·44 cm^{-1}. $R = 0{\cdot}049$ for 966 reflections. The main-chain structure is similar to that of *tert*-butyloxycarbonyl-sarcosylglycine benzyl ester. The

conformations of the *trans*-sarcosyl residues in peptides are classified into two types on the basis of the torsion angles (φ,ψ); in type I $\varphi = -60$ to $-100°$ and $\psi = 170 \pm 25°$, and in type II $\varphi = -120$ to $-135°$ and $\psi = 65$ to $70°$, the enantiomorphs with negative φ being considered. The present sarcosyl residue belongs to type I.

Introduction. *tert*-Butyloxycarbonyl-L-prolylsarcosine (Boc-Pro-Sar) was prepared and crystallized from an ethyl acetate solution. The intensity data were collected on a Rigaku automated diffractometer with Ni-filtered Cu $K\alpha$ radiation. A crystal with dimensions 0·3 × 0·15 × 0·01 mm was selected, and 966 reflections with $2\theta \leq 100°$ were obtained by the θ–2θ scan method. The intensity data were corrected for Lorentz and polarization effects.

The structure was solved by the use of *MULTAN* (Germain, Main & Woolfson, 1971). The refinement was carried out by the block-diagonal least-squares method using *HBLS* (Ashida, 1973). In the refinement, the weights $w = a$ for $|F_o| = 0$ and $w = [\sigma^2(F) + b|F_o| + c|F_o|^2]^{-1}$ were assigned, where $\sigma(F)$ is the standard deviation based on counting statistics. The final refinement ($a = 0{\cdot}383$, $b = -0{\cdot}061$ and $c = 0{\cdot}004$) gave the R value of 0·049 (0·042 for 909 non-zero reflections). The temperature factors were anisotropic for the non-hydrogen atoms and isotropic for the H atoms. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All the calculations were carried out on a FACOM 230-60 computer at Nagoya University. The final atomic parameters are listed in Table 1.*

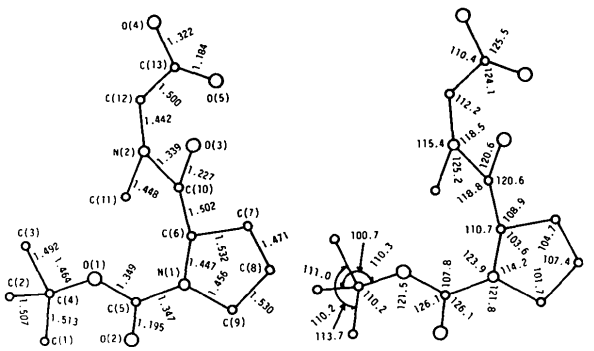

Fig. 1. Bond distances (Å) and angles (°).

Table 1. *Positional parameters* ($\times 10^4$) *with their standard deviations in parentheses*

	x	*y*	*z*
C(1)	7732 (3)	2567 (3)	565 (9)
C(2)	6358 (4)	2330 (3)	2837 (7)
C(3)	6078 (5)	2352 (3)	−824 (7)
C(4)	6666 (3)	2678 (2)	855 (7)
C(5)	6633 (3)	4075 (2)	−234 (6)
C(6)	5795 (3)	4883 (2)	2313 (6)
C(7)	5692 (3)	5788 (3)	2515 (10)
C(8)	5806 (3)	6094 (3)	460 (9)
C(9)	6468 (3)	5519 (3)	−658 (9)
C(10)	4816 (3)	4520 (2)	2120 (5)
C(11)	4773 (4)	4278 (4)	5783 (7)
C(12)	3391 (3)	4012 (3)	3639 (6)
C(13)	2728 (3)	4690 (2)	4108 (5)
N(1)	6331 (2)	4785 (2)	471 (5)
N(2)	4383 (2)	4243 (2)	3772 (5)
O(1)	6444 (2)	3520 (2)	1178 (4)
O(2)	7013 (2)	3960 (2)	−1814 (5)
O(3)	4411 (2)	4496 (2)	488 (4)
O(4)	1838 (2)	4430 (2)	4284 (5)
O(5)	2977 (2)	5360 (2)	4281 (5)

Discussion. The bond distances and angles involving non-hydrogen atoms are shown in Fig. 1. The average e.s.d.'s of the distances and angles are 0·007 Å and 0·3°, respectively. The equations of the best planes and the related data are listed in Table 2. The torsion angles are compared in Fig. 2, with those of Boc-Sar-Gly-OBz (Itoh, Yamane, Ashida, Sugihara, Imanishi & Higashimura, 1976). The two peptides have essentially the same main-chain structure. The definition of the torsion angles given by the IUPAC–IUB Commission on Biochemical Nomenclature (1970) has been adopted.

* Lists of the anisotropic thermal parameters, parameters of hydrogen atoms and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33506 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

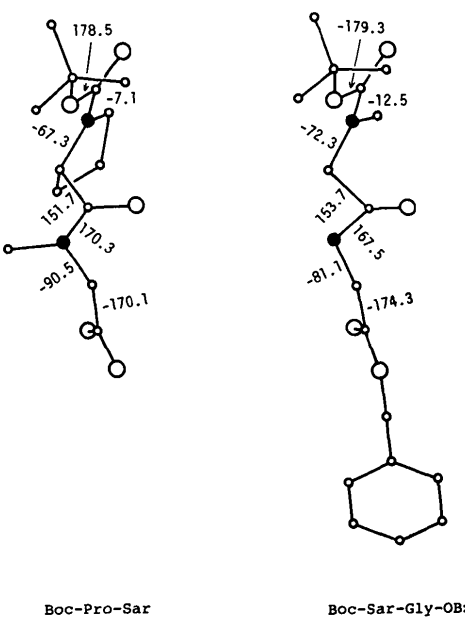

Fig. 2. Torsion angles (°) of the molecule. The torsion angles of Boc-Sar-Gly-OBz (Itoh *et al.*, 1976) are also shown.

Table 2. *Best planes*

(*a*) Equations of the best planes

$X = ax$, $Y = by$, $Z = cz$

I	$-0{\cdot}8778X - 0{\cdot}1538Y - 0{\cdot}4537Z + 9{\cdot}1201 = 0$	Amide Boc-Pro
II	$0{\cdot}3606X - 0{\cdot}9204Y - 0{\cdot}1514Z + 4{\cdot}7934 = 0$	Peptide Pro-Sar
III	$-0{\cdot}1460X + 0{\cdot}1477Y - 0{\cdot}9782Z + 2{\cdot}0698 = 0$	Carboxyl Sar
IV	$-0{\cdot}8844X - 0{\cdot}0878Y - 0{\cdot}4584Z + 8{\cdot}6287 = 0$	Pro ring

(*b*) Dihedral angles (°) between the planes

	I	II	III
II	96·1		
III	56·7	92·3	
IV	3·8	99·7	55·6

(*c*) Displacements ($\times 10^3$ Å) of atoms from the planes

I		II		III		IV	
C(5)	6	C(6)	−61	C(12)	1	C(6)	43
C(6)	54	C(10)	26	C(13)	−2	C(7)	−25
C(9)	−37	C(11)	7	O(4)	1	C(9)	25
N(1)	−21	C(12)	−61	O(5)	1	N(1)	−42
O(1)	−47	N(2)	68	H(22)*	38	C(5)*	−95
O(2)	46	O(3)	24	N(2)*	−231	C(8)*	417
C(4)*	−4	C(7)*	−1532			C(10)*	1364
C(7)*	−114	C(13)*	−1490				
C(8)*	289	N(1)*	546				
C(10)*	1406						

* Atoms not included in the best-plane calculations.

Table 3. *Torsion angles* (°) *of the trans-sarcosyl residues*

The enantiomorphs with negative φ are listed.

	Reference	ω	φ	ψ	Type
Boc-L-Pro-Sar	1	170·3	−90·5	−170·1	I
cyclo(Sar)$_4$	2	170·6	−120·8	65·5	II
cyclo(Sar)$_5$	3	179·1	−122·7	70·0	II
		161·7	−63·6	147·7	I
cyclo[L-Ala-(Sar)$_4$]	4	163·1	−68·1	141·3	I
cyclo(Sar)$_7$	5	−175·9	−134·4	68·7	II
		−179·8	−87·4	−175·7	I
		161·2	−63·8	−168·7	I
cyclo(Sar)$_8$	6	169·7	−71·0	167·7	I
		178·2	−93·1	179·4	I
		171·7	−77·5	173·0	I
		173·9	−83·1	172·5	I

References: (1) This study; (2) Groth (1970); (3) Groth (1973*b*); (4) Groth (1974); (5) Groth (1975); (6) Groth (1973*a*).

The linkage between Boc and the Pro residue has a *cis* conformation. The structure of this linkage shows good agreement with those in Boc-L-Pro-L-Pro-L-Pro-L-Pro-OBz (Matsuzaki, 1974) and Aoc-L-Pro-L-Pro-L-Pro (Kartha, Ashida & Kakudo, 1974), where Aoc is an amyloxycarbonyl group. The *cis* conformation in the linkage between Boc and the N-substituted amino acid residue is also found in Boc-Sar-Gly-OBz (Itoh *et al.*, 1976).

The peptide bond between the Pro and Sar residues is *trans*. The (φ,ψ) pair of the Sar residue involved in the *trans* peptide linkages may be classified into two types, as shown in Table 3. In type I, φ ranges from −60 to −100° and ψ is distributed around 170° (145 to 190°), and in type II, φ ranges from −120 to −135° and ψ is roughly 70°, only the enantiomorphs with negative φ being considered. The Sar residue in this peptide (−90·5, −170·1°) belongs to type I. Thus the structural role of the methyl group of Sar in the peptides is similar to that of the pyrrolidine ring in the Pro peptides.

The torsion angles of the pyrrolidine ring are: $\theta = -7{\cdot}9$, $\chi_1 = 22{\cdot}9$, $\chi_2 = -29{\cdot}8$, $\chi_3 = 24{\cdot}5$, $\chi_4 = -9{\cdot}7°$. The pyrrolidine ring takes a puckered form with the C_2–C^γ-*endo* conformation (Ashida & Kakudo, 1974).

A hydrogen bond is formed between O(4) and O(3) ($\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$), with the geometry of O···O 2·635, H···O 1·67 Å and ∠O–H···O 165°.

The authors express their thanks to Professor M. Kakudo of Osaka University, who kindly allowed them to use the diffractometer in his laboratory.

References

ASHIDA, T. (1973). *The Universal Crystallographic Computing System – Osaka*, pp. 55–61. The Computation Center, Univ. of Osaka, Japan.

ASHIDA, T. & KAKUDO, M. (1974). *Bull. Chem. Soc. Jpn*, **47**, 1129–1133.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

GROTH, P. (1970). *Acta Chem. Scand.* **24**, 780–790.

GROTH, P. (1973*a*). *Acta Chem. Scand.* **27**, 3217–3226.

GROTH, P. (1973*b*). *Acta Chem. Scand.* **27**, 3419–3426.

GROTH, P. (1974). *Acta Chem. Scand. Ser. A*, **28**, 449–454.

GROTH, P. (1975). *Acta Chem. Scand. Ser. A*, **29**, 38–44.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–73. Birmingham: Kynoch Press.

ITOH, H., YAMANE, T., ASHIDA, T., SUGIHARA, T., IMANISHI, Y. & HIGASHIMURA, T. (1976). *Acta Cryst.* B**32**, 3355–3357.

IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *J. Mol. Biol.* **52**, 1–17.

KARTHA, G., ASHIDA, T. & KAKUDO, M. (1974). *Acta Cryst.* B**30**, 1861–1866.

MATSUZAKI, T. (1974). *Acta Cryst.* B**30**, 1029–1036.

Acta Cryst. (1978). B**34**, 2643–2645

Ammonium Hydrogen 1-Malate

BY W. VERSICHEL, W. VAN DE MIEROOP AND A. T. H. LENSTRA*

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium

(*Received* 7 *March* 1978; *accepted* 5 *April* 1978)

Abstract. $(NH_4)^+(C_4H_5O_5)^-$. $P2_12_12_1$, $a = 7{\cdot}625$ (3), $b = 8{\cdot}106$ (4), $c = 10{\cdot}607$ (4) Å, $Z = 4$, $D_c = 1{\cdot}703$, $D_m = 1{\cdot}69$ g cm^{-3}, $\mu = 1{\cdot}53$ cm^{-1}. The conformation of the hydrogen malate is different from that found in the corresponding Ni^{2+} salt. This is due to complex formation in the latter compound between the Ni^{2+} ion and the alcoholic OH groups. In the crystal structure of the NH_4 salt all non-aliphatic hydrogen atoms participate in hydrogen bonding.

Introduction. The crystals of ammonium hydrogen malate were grown at room temperature by slow evaporation of a water solution. Reflections were measured on an Enraf–Nonius CAD-4 computer-automated four-circle diffractometer, using Mo $K\alpha$ radiation and a graphite monochromator ($2\theta = 12{\cdot}6°$). From the systematic extinctions the space group $P2_12_12_1$ was inferred. Intensities up to $\theta = 30°$ were measured. For time economy, 978 reflections were retained with $I > 2\sigma(I)$. No absorption or extinction corrections were applied. The structure was solved by direct methods using the *MULTAN* program of Germain, Main & Woolfson (1971). An E map with 196 terms showed all non-hydrogen atoms. After refinement of the related atomic parameters, a difference Fourier map revealed the positions of all hydrogen atoms.

The structure was refined by block-diagonal least-squares calculations, in which each reflection was given a weight based on the counting statistics. The final difference Fourier map showed no maxima above the level of 0·15 e Å^{-3}. The positional parameters resulting from this procedure are presented in Table 1.† The positional parameters given correspond to the absolute configuration (S) of the malate ion.

* Author to whom correspondence should be addressed.

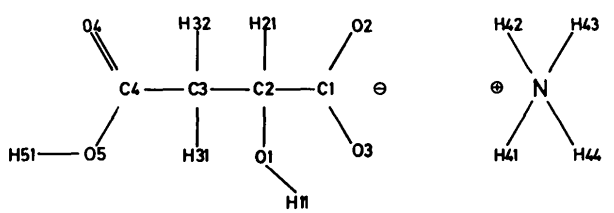

Fig. 1. Numbering of the atoms in ammonium hydrogen malate.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33535 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates of ammonium hydrogen 1-malate*

x, *y* and *z* are given as fractional coordinates. The e.s.d. (in parentheses) refers to the last significant digit of the parameter.

	x	*y*	*z*
N	0·9260 (2)	0·8697 (2)	0·0357 (1)
C(1)	0·5446 (2)	0·8585 (3)	0·2587 (2)
C(2)	0·3496 (2)	0·9055 (3)	0·2672 (2)
C(3)	0·2513 (2)	0·7834 (3)	0·3496 (2)
C(4)	0·0708 (2)	0·8479 (3)	0·3786 (2)
O(1)	0·2681 (2)	0·9054 (2)	0·1476 (1)
O(2)	0·6321 (2)	0·8731 (2)	0·3586 (1)
O(3)	0·6032 (2)	0·8108 (2)	0·1564 (1)
O(4)	0·0431 (2)	0·9650 (2)	0·4455 (1)
O(5)	−0·0541 (2)	0·7620 (2)	0·3248 (1)
H(11)	0·334 (3)	0·951 (2)	0·091 (2)
H(21)	0·343 (2)	1·008 (2)	0·301 (1)
H(31)	0·246 (2)	0·676 (2)	0·310 (2)
H(32)	0·311 (2)	0·770 (2)	0·427 (2)
H(41)	0·895 (3)	1·001 (3)	−0·024 (2)
H(42)	0·835 (3)	0·838 (2)	0·075 (2)
H(43)	1·008 (2)	0·896 (3)	0·082 (2)
H(44)	0·960 (3)	0·781 (2)	−0·009 (2)
H(51)	−0·169 (3)	0·817 (2)	0·342 (2)