Acta Cryst. (1995). C**51**, 537–538

N-[2(*R*)-Bromopropanoyl]-(2*S*)-proline Methyl Ester

SCOTT L. INGHAM†

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

MORAG M. LENMAN

Chemistry Department, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland

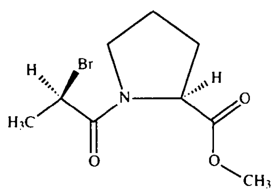
(*Received* 30 *March* 1994; *accepted* 7 *July* 1994)

Abstract

The structure and absolute configuration of the title compound, $C_9H_{14}BrNO_3$, have been determined and are reported here.

Comment

The substituted peptide *N*-[2(*R*)-bromopropanoyl]-(2*S*)-proline methyl ester, (I), has been structurally characterized and the absolute configuration of the two chiral centres determined.



(I)

The amide bond of the peptide shows a significant degree of double-bond character [N—C(3) 1.346 (7) Å] as a result of the delocalization of the N-atom lone pair with the adjacent carbonyl group. The angles about the N atom reflect this delocalization; observed values are 113.1 (5), 117.8 (5) and 128.3 (5)°. This type of delocalization is also exhibited in the C—O bond of the methyl ester, where the ester O atom, O3, forms bonds of length 1.334 (7) and 1.428 (8) Å with the carbonyl and methyl atoms C8 and C9, respectively. All other distances and angles are generally as expected. The bond lengths observed for (I) are in accordance with those observed for the closely related compound *N*-(*S*)-α-bromophenylacetyl-(*S*)-proline methyl ester (Smits, Beurskens, Zeegers & Ottenheijm, 1986). In that compound the absolute configuration of the chiral centre to which the Br atom is attached was determined to be (*S*), whereas in (I) this centre has the (*R*) configuration. The bond lengths of the methyl ester and the proline moieties correspond well with values found in pivaloyl-L-prolyl-D-proline methyl ester (Benedetti, Bavoso, di Blasio, Pavone, Pedone, Toniolo & Bonora, 1982) and *N*-*tert*-butoxycarbonyl-D-prolyl-L-prolyl-D-prolyl methyl ester (Giordano, De Santis & Silva, 1990). The torsion angles C7—N—C3—C2 and C3—N—C7—C8, which describe the geometry about the peptide, are −173.3 (5) and −71.2 (6)°, respectively.

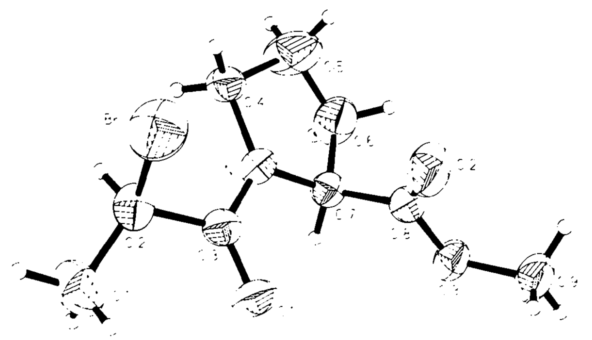


Fig. 1. Structure of (I) showing 50% probability displacement ellipsoids.

Experimental

Crystal data

$C_9H_{14}BrNO_3$	Mo $K\alpha$ radiation
$M_r = 264.12$	$\lambda = 0.71073$ Å
Trigonal	Cell parameters from 25 reflections
$P3_2$	$\theta = 16.97–18.68°$
$a = 9.793$ (1) Å	$\mu = 3.703$ mm^{-1}
$c = 9.978$ (2) Å	$T = 293$ (10) K
$V = 828.7$ (2) Å^3	Needle
$Z = 3$	0.50 × 0.25 × 0.15 mm
$D_x = 1.588$ Mg m^{-3}	Colourless
	Crystal source: crystallized from MeOH–pentane

Data collection

Rigaku AFC-7*R* diffractometer	$R_{int} = 0.0234$
$\omega 2\theta$ scans	$\theta_{max} = 24.97°$
Absorption correction: semi-empirical (ψ scans)	$h = -11 \rightarrow 10$
$T_{min} = 0.666$, $T_{max} = 0.999$	$k = 0 \rightarrow 11$
1634 measured reflections	$l = 0 \rightarrow 11$
1029 independent reflections	3 standard reflections monitored every 100 reflections
940 observed reflections [$I > 2\sigma(I)$]	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.0343$	$\Delta\rho_{max} = 0.343$ e Å^{-3}
$wR(F^2) = 0.0909$	$\Delta\rho_{min} = -0.258$ e Å^{-3}

† Present address: The University of Edinburgh, King's Buildings, West Mains Raod, Edinburgh EH9 3JJ, Scotland.

$S = 1.140$
1029 reflections
129 parameters
H atom refined with a riding model
$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 0.4771P]$
where $P = (F_o^2 + 2F_c^2)/3$
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Br	−0.21052 (10)	0.19080 (9)	−0.00055 (8)	0.0712 (3)
O1	−0.0925 (5)	−0.0922 (5)	0.0758 (5)	0.0479 (10)
O2	−0.4777 (7)	−0.3416 (6)	0.0274 (6)	0.0642 (15)
O3	−0.3892 (5)	−0.4940 (5)	0.1089 (5)	0.0474 (10)
N	−0.2783 (5)	−0.1059 (5)	0.2138 (5)	0.0361 (10)
C1	0.0882 (9)	0.2359 (9)	0.0767 (10)	0.066 (2)
C2	−0.0779 (7)	0.1528 (7)	0.1240 (6)	0.0438 (13)
C3	−0.1501 (7)	−0.0258 (7)	0.1358 (6)	0.0359 (12)
C4	−0.3553 (7)	−0.0435 (8)	0.2990 (7)	0.0435 (14)
C5	−0.4918 (11)	−0.1912 (11)	0.3543 (10)	0.081 (3)
C6	−0.4526 (10)	−0.3149 (9)	0.3501 (8)	0.065 (2)
C7	−0.3353 (7)	−0.2725 (7)	0.2363 (6)	0.0379 (13)
C8	−0.4105 (6)	−0.3697 (6)	0.1108 (6)	0.0386 (13)
C9	−0.4633 (9)	−0.6029 (8)	0.0014 (8)	0.061 (2)

Table 2. *Selected geometric parameters* (Å, °)

Br—C2	1.963 (6)	N—C3	1.346 (7)
O1—C3	1.211 (7)	N—C7	1.453 (7)
O2—C8	1.175 (8)	N—C4	1.458 (8)
O3—C8	1.334 (7)	C2—C3	1.529 (8)
O3—C9	1.428 (8)		
C3—N—C7	117.8 (5)	C7—N—C4	113.1 (5)
C3—N—C4	128.3 (5)		
C7—N—C3—C2	−173.3 (5)	C3—N—C7—C8	−71.2 (6)

Since (I) crystallizes in a polar space group, polar axis restraints were applied by the method of Flack & Schwarzenbach (1988) and the absolute structure of the crystal used for the investigation was established as described by Flack (1983).

Data collection: *MSC CTR* (Molecular Structure Corporation, 1991). Cell refinement: *MSC CTR*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL*93.

We would like to acknowledge Dr P. R. Raithby for kindly allowing the use of a diffractometer for data collection.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HU1118). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Benedetti, E., Bavoso, A., di Blasio, B., Pavone, V., Pedone, C., Toniolo, C. & Bonora, G. M. (1982). *Int. J. Pept. Protein Res.* **20**, 312–319.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Flack, H. D. & Schwarzenbach, D. (1988). *Acta Cryst.* A**44**, 499–506.
Giordano, F., De Santis, P. & Silva, A. M. (1990). *Acta Cryst.* C**46**, 2185–2189.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1991). *MSC CTR*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
Smits, J. M. M., Beurskens, P. T., Zeegers, B. & Ottenheijm, H. C. J. (1986). *J. Crystallogr. Spectrosc. Res.* **16**, 739–746.

Acta Cryst. (1995). C**51**, 538–541

A Thiourea–1,5-Cyclooctadiene Clathrate at 173 K

Isabelle Garneau, Stéphane Raymond and François Brisse

Département de Chimie, Université de Montréal, CP 6128, Succ. A, Montréal, Québec, Canada H3C 3J7

(*Received* 18 *November* 1993; *accepted* 4 *July* 1994)

Abstract

The structure of the host–guest-type clathrate, thiourea–1,5-cyclooctadiene (3/1) $3CH_4N_2S.C_8H_{12}$, at 173 K, is reported. The thiourea molecules (host) form nearly hexagonal channels while the ordered 1,5-cyclooctadiene guest molecules occupy the channels. The channels result from hydrogen bonding between thiourea molecules. The channel axis is parallel to the *ac* bisector. Although the guest molecules are well defined, there seems to be slight orientational disorder about their centre of mass.

Comment

A great many studies (Schiessler & Flitter, 1952; Hagan, 1962; Fetterly, 1964) on inclusion compounds formed between urea or thiourea and guest molecules have been undertaken since the accidental discovery of such adducts by Bengen (1940). Urea and thiourea form, through an extensive network of hydrogen bonds, hexagonal channels much like a honeycomb. The guest molecules find their place in these channels. The urea channels are small and can only accommodate linear aliphatic molecules or polymers such as polyethers (Chenite & Brisse, 1991, 1992) or