

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## (7a*S*)-(-)-Dimethyl(1-oxido-3-oxo-5,6,7,7a-tetrahydro-3*H*-pyrrolizin-2-yl)-sulfonium

Leonardo Gutiérrez-Lazcano,<sup>a</sup> Joel L. Terán,<sup>a</sup> Jorge R. Juárez,<sup>a</sup> Marcos Flores-Alamo<sup>b</sup> and Angel Mendoza<sup>a\*</sup>

<sup>a</sup>Centro de Química, Instituto de Ciencias, Benemérita Universidad Autónoma de Puebla, Puebla, Pue., Mexico, and <sup>b</sup>Facultad de Química, Universidad Nacional Autónoma de México, 04510 México, DF, Mexico  
Correspondence e-mail: angel.mendoza.m@gmail.com

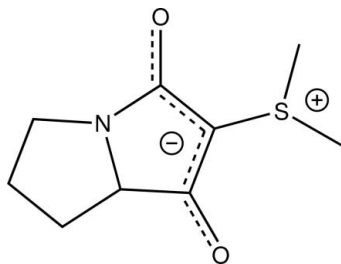
Received 18 January 2012; accepted 27 January 2012

Key indicators: single-crystal X-ray study;  $T = 130$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.027;  $wR$  factor = 0.065; data-to-parameter ratio = 15.6.

In the zwitterionic title compound,  $\text{C}_9\text{H}_{13}\text{NO}_2\text{S}$ , the pyrrolidine heterocycle adopts an envelope conformation (with the C atom in the 7-position as the flap). The negative charge is delocalized over the two carbonyl groups and the C atom connecting them. The positive charge is located on the S atom. Two intermolecular  $\text{C}-\text{H}\cdots\text{O}$  interactions are observed. The molecular geometry at the S atom is trigonal pyramidal.

### Related literature

For background to the synthesis of chiral non-racemic zwitterionic compounds, see: Zang *et al.* (2008); Kappe *et al.* (1983); Palillero *et al.* (2009). For the biological activity of related structures, see: Basco *et al.* (1994); Koruznjak *et al.* (2003). For puckering parameters, see: Cremer & Pople (1975).



### Experimental

#### Crystal data

$\text{C}_9\text{H}_{13}\text{NO}_2\text{S}$   
 $M_r = 199.26$   
 Orthorhombic,  $P2_12_12_1$   
 $a = 5.8761$  (3) Å  
 $b = 9.0858$  (5) Å  
 $c = 17.7107$  (9) Å  
 $V = 945.56$  (9) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.31$  mm<sup>-1</sup>  
 $T = 130$  K  
 $0.46 \times 0.33 \times 0.07$  mm

#### Data collection

Oxford Xcalibur Atlas Gemini diffractometer  
 Absorption correction: analytical (*CrysAlis PRO*; Oxford Diffraction, 2009)  
 $T_{\min} = 0.895$ ,  $T_{\max} = 0.976$   
 6356 measured reflections  
 1873 independent reflections  
 1736 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.037$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$   
 $wR(F^2) = 0.065$   
 $S = 1.04$   
 1873 reflections  
 120 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.20$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.26$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983), with 758 Friedel pairs  
 Flack parameter:  $-0.07$  (7)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C4}-\text{H4}\cdots\text{O2}^{\text{i}}$	1.00	2.55	3.4145 (19)	145
$\text{C7}-\text{H7B}\cdots\text{O1}^{\text{ii}}$	0.99	2.59	3.570 (2)	173

Symmetry codes: (i)  $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$ .

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors are grateful to BUAP (Project VIEP 2011) for financial support. LGL thanks VIEP for a scholarship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5793).

### References

- Basco, L. K., Mitaku, S., Skaltsounis, A. L., Ravelomanantsoa, N., Tillequin, F., Koch, M. & Le Bras, J. (1994). *Antimicrob. Agents Chemother.* **38**, 1169–1171.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Kappe, T., Korbuuly, G. & Pongratz, E. (1983). *Monatsh. Chem.* **114**, 303–315.
- Koruznjak, J. D., Grdisa, M., Slade, N., Zamola, B., Pavelic, K. & Karminski-Zamola, G. (2003). *J. Med. Chem.* **46**, 4516–4524.
- Oxford Diffraction (2009). *CrysAlis PRO and CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Palillero, A., Terán, J. L., Gnecco, D., Juárez, J. R., Orea, M. L. & Castro, A. (2009). *Tetrahedron Lett.* **50**, 4208–4211.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Zang, S. L., Huang, Z. S., Li, Y. M., Chan, A. S. C. & Gu, L. Q. (2008). *Tetrahedron*, **64**, 4403–4407.

## supporting information

*Acta Cryst.* (2012). E68, o752 [doi:10.1107/S1600536812003601]

**(7a*S*)-(-)-Dimethyl(1-oxido-3-oxo-5,6,7,7a-tetrahydro-3*H*-pyrrolizin-2-yl)sulfonium**

**Leonardo Gutiérrez-Lazcano, Joel L. Terán, Jorge R. Juárez, Marcos Flores-Alamo and Angel Mendoza**

**S1. Comment**

The synthesis of chiral non racemic zwitterionic compounds is an original area of interest in organic chemistry (Zang *et al.*, 2008; Kappe *et al.*, 1983) because they are useful intermediates for the synthesis of diverse interesting nitrogen heterocyclic compounds (Palillero *et al.*, 2009) with interesting biological properties (Basco *et al.*, 1994; Koruznjak *et al.*, 2003).

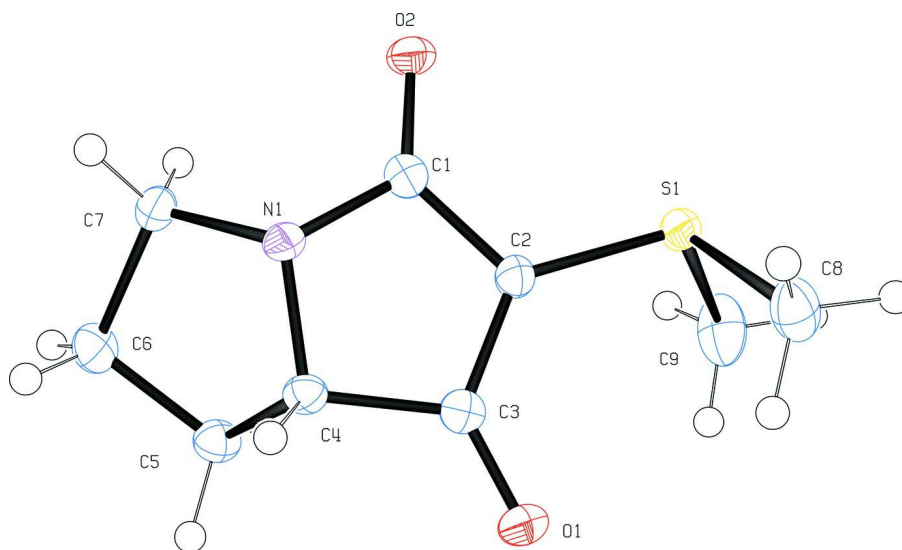
In the title zwitterionic compound, C<sub>19</sub>H<sub>13</sub>NO<sub>2</sub>S, the chiral centre shows an *S* configuration, and the five membered pyrrolidine heterocycle shows an envelope conformations on C5 with puckering parameters (Cremer & Pople, 1975)  $\varphi_2 = 258.4$  (3)° and  $q_2 = 0.4038$  (19) Å. The five membered ring N1/C1/C2/C3/C4 shows a twist conformation on N1—C1 with puckering parameters  $\varphi_2 = 0.0903$  (18)° and  $q_2 = 22.4$  (12) Å. The bond distances of C1—O2 [1.235 (2) Å] and C3—O1 [1.238 (2) Å] are similar as in related systems which were previously reported. The C2—C3 bond distance [1.406 (2) Å] has the same length as an aromatic bond and C2—C1 [1.435 (2) Å] is shorter than a typical *sp*<sup>3</sup>—*sp*<sup>3</sup> bond distance. This suggests, that the negative charge is delocalized on the O1/C3/C2/C2/O2 system. Two intermolecular weak interactions C4—H4···O2 (3.412 (2) Å) and C7—H7B···O1 (3.570 (2) Å) are observed.

**S2. Experimental**

The title compound, was obtained by an intramolecular cyclization reaction of (*S*)-(-)-[2-(2-Methoxycarbonyl-pyrrolidin-1-yl)-2-oxo-ethyl]-dimethyl-sulfonium; bromide (1 mmol), which was dissolved in CH<sub>3</sub>CN (10 ml), treated with KOH (1.2 mmol) and stirred for 2 h at room temperature. The resulting mixture was concentrated in vacuum and dissolved in ethyl acetate, filtered and concentrated giving the desired compound in 98%. Crystals were obtained from an ethyl acetate/diethyl ether solution; m.p. 110–112 °C,  $[\alpha]_D^{25} = -13.4$  (*c* 1.0, CH<sub>2</sub>Cl<sub>2</sub>). IR (KBr) 3447, 1655, 1591, 1372 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(p.p.m., *J*Hz): 1.51 (m, 1H), 2.05 (m, 3H), 2.99 (s, 3H), 3.01 (s, 3H), 3.12 (m, 1H), 3.57 (td, *J* = 7.8, 11.0 Hz, 1H), 3.85 (dd, *J* = 7.24, 9.28 Hz, 1H). HRMS (FAB<sup>+</sup>): Calcd for C<sub>9</sub>H<sub>13</sub>NO<sub>2</sub>S: 199.0667. Found: 199.0665.

**S3. Refinement**

H atoms were placed in geometrically idealized positions and refined as riding on their parent atoms, with C—H distances fixed to 0.960 (methyl CH<sub>3</sub>) and 0.980 Å (methine CH) and with  $U_{iso}(H) = 1.5U_{eq}(methyl\ C)$  or  $1.2U_{eq}(C)$ .

**Figure 1**

The molecular structure of title compound, with atom labels and 50% probability displacement ellipsoids for non-H atoms.

**(7aS)-(-)-Dimethyl(1-oxido-3-oxo-5,6,7,7a-tetrahydro-3H-pyrrolizin-2-yl)sulfonium**

*Crystal data*

$C_9H_{13}NO_2S$

$M_r = 199.26$

Orthorhombic,  $P2_12_12_1$

$a = 5.8761$  (3) Å

$b = 9.0858$  (5) Å

$c = 17.7107$  (9) Å

$V = 945.56$  (9) Å<sup>3</sup>

$Z = 4$

$F(000) = 424$

$D_x = 1.406$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4129 reflections

$\theta = 3.5\text{--}26.0^\circ$

$\mu = 0.31$  mm<sup>-1</sup>

$T = 130$  K

Plate, colourless

$0.46 \times 0.33 \times 0.07$  mm

*Data collection*

Oxford Xcalibur Atlas Gemini  
diffractometer

Graphite monochromator

Detector resolution: 10.4685 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: analytical

(*CrysAlis PRO*; Oxford Diffraction, 2002)

$T_{\min} = 0.895$ ,  $T_{\max} = 0.976$

6356 measured reflections

1873 independent reflections

1736 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 26.1^\circ$ ,  $\theta_{\min} = 3.7^\circ$

$h = -7 \rightarrow 7$

$k = -10 \rightarrow 11$

$l = -18 \rightarrow 21$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.065$

$S = 1.04$

1873 reflections

120 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.20 \text{ e } \text{Å}^{-3}$

$$\Delta\rho_{\min} = -0.26 \text{ e } \text{Å}^{-3}$$

Absolute structure: Flack (1983), with 758  
 Friedel pairs  
 Absolute structure parameter:  $-0.07 (7)$

*Special details*

**Geometry.** All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.72287 (7)	0.59085 (4)	0.01093 (2)	0.01852 (12)
O1	0.6977 (3)	0.26576 (13)	0.09183 (7)	0.0293 (3)
O2	0.4048 (2)	0.74463 (12)	0.13031 (6)	0.0229 (3)
N1	0.4198 (2)	0.53624 (15)	0.20467 (8)	0.0172 (3)
C1	0.4721 (3)	0.61719 (18)	0.14100 (9)	0.0172 (4)
C2	0.6056 (3)	0.52340 (19)	0.09255 (9)	0.0188 (4)
C3	0.6092 (3)	0.37738 (18)	0.11921 (10)	0.0193 (4)
C4	0.4806 (3)	0.38002 (17)	0.19391 (9)	0.0173 (4)
H4	0.5823	0.3464	0.2358	0.021*
C5	0.2519 (3)	0.30179 (17)	0.19885 (10)	0.0216 (4)
H5A	0.2702	0.1975	0.2138	0.026*
H5B	0.1682	0.3069	0.1504	0.026*
C6	0.1329 (3)	0.3908 (2)	0.26032 (10)	0.0228 (4)
H6A	0.1871	0.3614	0.3111	0.027*
H6B	-0.0341	0.3772	0.2579	0.027*
C7	0.1984 (3)	0.55113 (19)	0.24287 (10)	0.0222 (4)
H7A	0.0847	0.5982	0.2094	0.027*
H7B	0.2125	0.6096	0.2898	0.027*
C8	1.0123 (3)	0.5311 (2)	0.01195 (12)	0.0296 (4)
H8A	1.0832	0.5535	-0.0368	0.044*
H8B	1.0179	0.4248	0.0209	0.044*
H8C	1.0946	0.5823	0.0523	0.044*
C9	0.6187 (4)	0.4744 (3)	-0.06291 (11)	0.0370 (5)
H9A	0.6929	0.5007	-0.1106	0.056*
H9B	0.4538	0.4873	-0.0679	0.056*
H9C	0.6523	0.3715	-0.0507	0.056*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0209 (2)	0.0186 (2)	0.0160 (2)	0.00209 (17)	0.00126 (16)	0.00138 (16)

O1	0.0388 (8)	0.0202 (6)	0.0290 (7)	0.0101 (6)	0.0091 (6)	0.0018 (5)
O2	0.0311 (7)	0.0156 (6)	0.0220 (6)	0.0036 (5)	0.0008 (6)	-0.0003 (5)
N1	0.0200 (8)	0.0147 (7)	0.0170 (7)	-0.0002 (6)	0.0002 (6)	-0.0023 (6)
C1	0.0173 (9)	0.0194 (9)	0.0150 (8)	-0.0035 (7)	-0.0038 (7)	-0.0014 (7)
C2	0.0205 (9)	0.0190 (8)	0.0169 (9)	0.0022 (8)	0.0023 (8)	0.0016 (7)
C3	0.0178 (9)	0.0193 (9)	0.0209 (9)	-0.0004 (7)	-0.0012 (7)	0.0003 (7)
C4	0.0176 (8)	0.0165 (8)	0.0179 (9)	0.0031 (7)	-0.0021 (7)	0.0013 (7)
C5	0.0213 (10)	0.0186 (8)	0.0250 (9)	-0.0018 (8)	-0.0005 (8)	-0.0005 (7)
C6	0.0166 (9)	0.0247 (10)	0.0272 (9)	-0.0060 (8)	0.0030 (7)	-0.0001 (8)
C7	0.0236 (10)	0.0210 (8)	0.0221 (9)	-0.0006 (8)	0.0067 (8)	-0.0029 (7)
C8	0.0191 (9)	0.0384 (10)	0.0314 (10)	0.0013 (8)	0.0018 (8)	0.0086 (9)
C9	0.0366 (13)	0.0563 (13)	0.0181 (10)	-0.0149 (11)	-0.0006 (9)	-0.0074 (10)

*Geometric parameters (Å, °)*

S1—C2	1.7146 (17)	C5—H5A	0.99
S1—C8	1.7851 (18)	C5—H5B	0.99
S1—C9	1.7900 (19)	C6—C7	1.538 (3)
O1—C3	1.238 (2)	C6—H6A	0.99
O2—C1	1.238 (2)	C6—H6B	0.99
N1—C1	1.381 (2)	C7—H7A	0.99
N1—C7	1.473 (2)	C7—H7B	0.99
N1—C4	1.476 (2)	C8—H8A	0.98
C1—C2	1.442 (2)	C8—H8B	0.98
C2—C3	1.408 (2)	C8—H8C	0.98
C3—C4	1.524 (2)	C9—H9A	0.98
C4—C5	1.523 (2)	C9—H9B	0.98
C4—H4	1	C9—H9C	0.98
C5—C6	1.526 (2)		
C2—S1—C8	105.40 (9)	H5A—C5—H5B	109.3
C2—S1—C9	105.50 (9)	C5—C6—C7	104.11 (14)
C8—S1—C9	98.84 (11)	C5—C6—H6A	110.9
C1—N1—C7	121.50 (14)	C7—C6—H6A	110.9
C1—N1—C4	110.68 (13)	C5—C6—H6B	110.9
C7—N1—C4	111.17 (13)	C7—C6—H6B	110.9
O2—C1—N1	123.51 (15)	H6A—C6—H6B	109
O2—C1—C2	129.47 (15)	N1—C7—C6	103.08 (13)
N1—C1—C2	106.99 (14)	N1—C7—H7A	111.1
C3—C2—C1	111.43 (15)	C6—C7—H7A	111.1
C3—C2—S1	127.84 (13)	N1—C7—H7B	111.1
C1—C2—S1	120.61 (13)	C6—C7—H7B	111.1
O1—C3—C2	130.27 (16)	H7A—C7—H7B	109.1
O1—C3—C4	124.12 (15)	S1—C8—H8A	109.5
C2—C3—C4	105.60 (14)	S1—C8—H8B	109.5
N1—C4—C5	103.19 (13)	H8A—C8—H8B	109.5
N1—C4—C3	104.31 (13)	S1—C8—H8C	109.5
C5—C4—C3	118.71 (14)	H8A—C8—H8C	109.5

N1—C4—H4	110	H8B—C8—H8C	109.5
C5—C4—H4	110	S1—C9—H9A	109.5
C3—C4—H4	110	S1—C9—H9B	109.5
C4—C5—C6	101.43 (13)	H9A—C9—H9B	109.5
C4—C5—H5A	111.5	S1—C9—H9C	109.5
C6—C5—H5A	111.5	H9A—C9—H9C	109.5
C4—C5—H5B	111.5	H9B—C9—H9C	109.5
C6—C5—H5B	111.5		
C7—N1—C1—O2	34.5 (2)	S1—C2—C3—C4	179.92 (13)
C4—N1—C1—O2	167.62 (15)	C1—N1—C4—C5	-116.83 (15)
C7—N1—C1—C2	-143.55 (15)	C7—N1—C4—C5	21.34 (17)
C4—N1—C1—C2	-10.39 (18)	C1—N1—C4—C3	7.84 (18)
O2—C1—C2—C3	-168.74 (17)	C7—N1—C4—C3	146.01 (13)
N1—C1—C2—C3	9.1 (2)	O1—C3—C4—N1	176.79 (16)
O2—C1—C2—S1	7.6 (3)	C2—C3—C4—N1	-2.07 (18)
N1—C1—C2—S1	-174.58 (12)	O1—C3—C4—C5	-69.1 (2)
C8—S1—C2—C3	-52.18 (19)	C2—C3—C4—C5	112.01 (16)
C9—S1—C2—C3	51.81 (19)	N1—C4—C5—C6	-37.44 (16)
C8—S1—C2—C1	132.16 (15)	C3—C4—C5—C6	-152.13 (15)
C9—S1—C2—C1	-123.85 (16)	C4—C5—C6—C7	40.51 (17)
C1—C2—C3—O1	177.13 (18)	C1—N1—C7—C6	136.85 (15)
S1—C2—C3—O1	1.1 (3)	C4—N1—C7—C6	3.89 (18)
C1—C2—C3—C4	-4.1 (2)	C5—C6—C7—N1	-27.69 (17)

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C4—H4 $\cdots$ O2 <sup>i</sup>	1.00	2.55	3.4145 (19)	145
C7—H7B $\cdots$ O1 <sup>ii</sup>	0.99	2.59	3.570 (2)	173

Symmetry codes: (i)  $-x+1, y-1/2, -z+1/2$ ; (ii)  $-x+1, y+1/2, -z+1/2$ .