Acta Crystallographica Section E
**Structure Reports**
**Online**
ISSN 1600-5368

# 2-Propyl 3,3-dibromo-2-hydroxypyrrolidine-1-carboxylate

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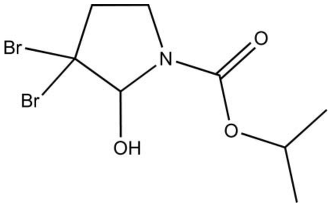
Received 29 January 2010; accepted 8 February 2010

Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.032; $wR$ factor = 0.082; data-to-parameter ratio = 69.4.

The title compound, $C_8H_{13}Br_2NO_3$, crystallizes as a non-merohedral twin with twin law −0.6 0 0.4/0 − 1 0 /1.6 0 0.6, and the structure has a refined twin domain ratio of 0.546 (5). The structure shows a compact conformation, with the ester unit roughly coplanar with a mean plane fitted through the non-H atoms of the pyrrolidine ring [dihedral angle = 8.23 (9)°]. In the crystal, inversion dimers linked by pairs of O—H⋯O hydrogen bonds generate an $R_2^2(12)$ motif.

## Related literature

For details of the synthesis, see: Magnus *et al.* (1994); Salamant & Hulme (2006). For puckering parameters, see: Cremer & Pople (1975). For hydrogen-bonding motifs, see: Bernstein *et al.* (1995).



## Experimental

### *Crystal data*

$C_8H_{13}Br_2NO_3$
$M_r$ = 331.01
Monoclinic, $P2_1/n$
$a$ = 10.1061 (5) Å
$b$ = 5.9914 (3) Å
$c$ = 18.5496 (9) Å
$\beta$ = 95.880 (2)°
$V$ = 1117.26 (10) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 7.24 mm$^{-1}$
$T$ = 100 K
0.44 × 0.16 × 0.11 mm

### *Data collection*

Bruker Kappa APEXII DUO CCD diffractometer
Absorption correction: multi-scan (TWINABS; Sheldrick, 1996) $T_{min}$ = 0.144, $T_{max}$ = 0.514
34994 measured reflections
9572 independent reflections
7956 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.042

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.082
$S$ = 1.03
9572 reflections
138 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.41 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.77 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| O1—H1*O*⋯O2$^i$ | 0.83 (3) | 1.92 (3) | 2.7479 (16) | 176 (3) |

Symmetry code: (i) $-x + 1, -y, -z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* and *CELL_NOW* (Sheldrick, 2004); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXTL* and local programs.

The diffractometer was purchased with funding from NSF grant No. CHE-0741837.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2278).

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# supplementary materials

*Acta Cryst.* (2010). E**66**, o597 [ **doi:10.1107/S1600536810005106** ]

## 2-Propyl 3,3-dibromo-2-hydroxypyrrolidine-1-carboxylate

**G. S. Nichol, S. Gunawan, Z. Xu, J. Dietrich and C. Hulme**

### Comment

We are working to develop new synthetic methodology by application of hypervalent iodine reagents (oxidation state III) in conjunction with bromotrimethylsilane (TMSBr). Specifically, iodosobenzene (Magnus *et al.*, 1994) or iodobenzenediacetate in the presence of TMSBr promotes controlled formation of an oxidized product in one pot, derived from cyclic amides. The transformation represents an α, β, β oxidative process, and the yield of the product, (I), was optimized by varying reaction parameters (Salamant & Hulme, 2006). The structure of this molecule generated from one simple microwave-assisted protocol was confirmed by X-ray crystallography.

The molecular structure of (I) is shown in Fig. 1. Molecular dimensions are unexceptional and the compound has a compact conformation; as evidenced by the torsion angle C2—N—C5—O2 = 0.1 (2)° the ester moiety is essentially coplanar with the pyrrolidine ring. Furthermore the angle between a least-squares plane fitted through all non-hydrogen atoms of the pyrrolidine ring (r.m.s. deviation = 0.1666 Å) and the ester moiety (r.m.s. deviation = 0.0226 Å) is 8.23 (9)°. The pyrrolidine ring adopts an envelope conformation with a Cremer–Pople puckering parameter Q of 0.4053 (15) Å (Cremer & Pople, 1975). The compound forms a hydrogen-bonded dimer by means of an $R^2_2(12)$ motif (Fig. 2; Bernstein *et al.*, 1995) although there is no further hydrogen bonding in the crystal structure.

### Experimental

To a solution of isopropyloxypyrrolidine (0.050 g, 0.318 mmol) in anhydrous dichloromethane (1 ml) was added iodobenzene diacetate (0.410 g, 1.272 mmol). Bromotrimethylsilane (0.330 ml, 2.540 mmol) was added dropwise and the mixture irradiated with a Biotage Initiator$^{TM}$ for 20 min at 120°C. The red-brown solution was then dissolved in EtOAc (25 ml) and quenched with 1M $Na_2S_2O_3$ (2 × 10 ml). The organic layer was washed with 1M $NaHCO_3$ (2 × 20 ml), saturated $Na_2CO_3$ (20 ml), brine solution (20 ml), and dried ($MgSO_4$). The solvent was evaporated in vacuo and purified by column chromatography ($CHCl_3$) to afford the α,β,β product (0.068 g, 0.207 mmol, 65%) as a white solid. MS (+ESI) *m/z* 354 $[M+Na]^+$

### Refinement

The crystal used was a two-component non-merohedral twin. The two components of the diffraction pattern were easily separated using CELL_NOW (Sheldrick, 2004) with twin law -0.6 0 0.4/0 -1 0 /1.6 0 0.6 and the structure has a refined twin scale factor of 0.546 (5). H atoms were identified from a difference Fourier map. The O—H H atom was freely refined with O—H = 0.83 (3) Å. C—H atoms were refined with $U_{iso}(H) = 1.5U_{eq}(C)$ (methyl) $U_{iso}(H) = 1.5U_{eq}(C)$ (all others) with constrained C—H distances in the range 0.98–1 Å.

## Figures

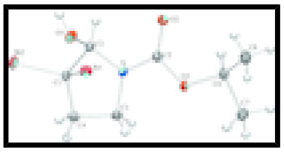

Fig. 1. The molecular structure of (I) with anisotropic displacement ellipsoids at the 50% probability level.

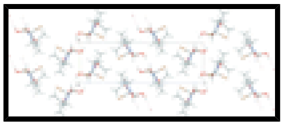

Fig. 2. An *a*-axis packing plot of (I). Blue dotted lines indicate hydrogen bonds; red dotted lines indicate hydrogen bond continuation.

## 2-Propyl 3,3-dibromo-2-hydroxypyrrolidine-1-carboxylate

### *Crystal data*

$C_8H_{13}Br_2NO_3$

$M_r = 331.01$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 10.1061$ (5) Å

$b = 5.9914$ (3) Å

$c = 18.5496$ (9) Å

$\beta = 95.880$ (2)°

$V = 1117.26$ (10) $Å^3$

$Z = 4$

$F(000) = 648$

$D_x = 1.968$ Mg $m^{-3}$

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

Cell parameters from 4995 reflections

$\theta = 2.2–36.3°$

$\mu = 7.24$ $mm^{-1}$

$T = 100$ K

Rod, colourless

0.44 × 0.16 × 0.11 mm

### *Data collection*

Bruker Kappa APEXII DUO CCD diffractometer

Radiation source: fine-focus sealed tube with Miracol optics

graphite

$\varphi$ and $\omega$ scans

Absorption correction: multi-scan (TWINABS; Sheldrick, 1996)

$T_{min} = 0.144$, $T_{max} = 0.514$

34994 measured reflections

9572 independent reflections

7956 reflections with $I > 2\sigma(I)$

$R_{int} = 0.042$

$\theta_{max} = 36.4°$, $\theta_{min} = 2.2°$

$h = -16 \rightarrow 16$

$k = 0 \rightarrow 9$

$l = 0 \rightarrow 30$

### *Refinement*

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.082$

$S = 1.03$

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 0.6397P]$

| | |
|---|---|
| | where $P = (F_o^2 + 2F_c^2)/3$ |
| 9572 reflections | $(\Delta/\sigma)_{max} < 0.001$ |
| 138 parameters | $\Delta\rho_{max} = 1.41$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -0.77$ e Å$^{-3}$ |

### *Special details*

**Experimental**. 1*H*- NMR (300 MHz, CDCl3) δ ppm 1.26 (d, J = 6.0 Hz, 6H), 2.78 (m, 1H), 3.00 (m, 1H), 3.55 (m, 2H), 4.65 (s, 1H), 5.00 (m, 1H), 5.66 (d, J = 18.6 Hz, 1H)

13 C-NMR (75 MHz, CDCl3) δ ppm 22.6, 43.4, 44.6, 64.9, 70.2, 77.9, 155.3

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > \sigma(F^2)$ 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$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.276925 (16) | 0.10387 (3) | 0.190848 (8) | 0.01807 (4) |
| Br2 | 0.113078 (15) | 0.17803 (3) | 0.039208 (9) | 0.01933 (4) |
| O1 | 0.39288 (12) | 0.2381 (2) | −0.01016 (6) | 0.01668 (19) |
| H1O | 0.371 (3) | 0.120 (5) | −0.0310 (15) | 0.029 (7)* |
| O2 | 0.68184 (12) | 0.16332 (19) | 0.07343 (7) | 0.0190 (2) |
| O3 | 0.69480 (10) | 0.47225 (18) | 0.14461 (6) | 0.01432 (18) |
| N | 0.49624 (12) | 0.3442 (2) | 0.10291 (7) | 0.0134 (2) |
| C1 | 0.27415 (14) | 0.2599 (2) | 0.09769 (7) | 0.0137 (2) |
| C2 | 0.40238 (14) | 0.1940 (2) | 0.06403 (7) | 0.0125 (2) |
| H2 | 0.4265 | 0.0345 | 0.0745 | 0.015* |
| C3 | 0.43486 (14) | 0.5339 (2) | 0.13709 (8) | 0.0153 (2) |
| H3A | 0.4716 | 0.6776 | 0.1219 | 0.018* |
| H3B | 0.4479 | 0.5230 | 0.1906 | 0.018* |
| C4 | 0.28818 (15) | 0.5100 (2) | 0.10886 (8) | 0.0156 (2) |
| H4A | 0.2297 | 0.5644 | 0.1448 | 0.019* |
| H4B | 0.2673 | 0.5919 | 0.0628 | 0.019* |
| C5 | 0.62874 (14) | 0.3155 (2) | 0.10427 (8) | 0.0137 (2) |
| C6 | 0.84008 (14) | 0.4710 (2) | 0.14715 (8) | 0.0146 (2) |
| H6 | 0.862 (2) | 0.423 (4) | 0.1000 (12) | 0.014 (5)* |
| C7 | 0.88361 (16) | 0.7097 (2) | 0.16218 (9) | 0.0185 (3) |
| H7A | 0.8399 | 0.8076 | 0.1247 | 0.028* |
| H7B | 0.9803 | 0.7206 | 0.1619 | 0.028* |
| H7C | 0.8588 | 0.7553 | 0.2097 | 0.028* |
| C8 | 0.89639 (17) | 0.3118 (3) | 0.20548 (10) | 0.0223 (3) |

| | | | | |
|---|---|---|---|---|
| H8A | 0.9936 | 0.3090 | 0.2069 | 0.033* |
| H8B | 0.8610 | 0.1617 | 0.1949 | 0.033* |
| H8C | 0.8711 | 0.3613 | 0.2525 | 0.033* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.02072 (7) | 0.02068 (7) | 0.01338 (6) | −0.00119 (5) | 0.00450 (5) | 0.00190 (5) |
| Br2 | 0.01232 (6) | 0.02662 (8) | 0.01853 (7) | −0.00274 (5) | −0.00098 (5) | −0.00543 (5) |
| O1 | 0.0195 (5) | 0.0195 (5) | 0.0112 (4) | −0.0029 (4) | 0.0021 (4) | −0.0022 (4) |
| O2 | 0.0149 (5) | 0.0183 (5) | 0.0239 (5) | 0.0008 (4) | 0.0017 (4) | −0.0089 (4) |
| O3 | 0.0113 (4) | 0.0153 (4) | 0.0160 (4) | −0.0003 (3) | −0.0004 (3) | −0.0044 (4) |
| N | 0.0116 (5) | 0.0136 (5) | 0.0150 (5) | −0.0012 (4) | 0.0007 (4) | −0.0046 (4) |
| C1 | 0.0126 (5) | 0.0162 (5) | 0.0119 (5) | −0.0013 (4) | −0.0003 (4) | −0.0009 (4) |
| C2 | 0.0120 (5) | 0.0142 (5) | 0.0113 (5) | −0.0017 (4) | 0.0016 (4) | −0.0021 (4) |
| C3 | 0.0142 (6) | 0.0137 (5) | 0.0179 (6) | 0.0002 (4) | 0.0018 (5) | −0.0047 (5) |
| C4 | 0.0148 (6) | 0.0145 (6) | 0.0173 (6) | 0.0018 (4) | 0.0010 (5) | −0.0021 (5) |
| C5 | 0.0127 (5) | 0.0149 (5) | 0.0132 (5) | 0.0000 (4) | 0.0004 (4) | −0.0014 (4) |
| C6 | 0.0106 (5) | 0.0160 (5) | 0.0170 (6) | −0.0002 (4) | 0.0009 (4) | −0.0011 (5) |
| C7 | 0.0160 (6) | 0.0165 (6) | 0.0226 (7) | −0.0032 (5) | −0.0006 (5) | 0.0003 (5) |
| C8 | 0.0187 (7) | 0.0180 (6) | 0.0286 (8) | 0.0002 (5) | −0.0052 (6) | 0.0022 (6) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Br1—C1 | 1.9624 (14) | C3—H3B | 0.990 |
| Br2—C1 | 1.9250 (14) | C3—C4 | 1.527 (2) |
| O1—H1O | 0.83 (3) | C4—H4A | 0.990 |
| O1—C2 | 1.3949 (17) | C4—H4B | 0.990 |
| O2—C5 | 1.2286 (18) | C6—H6 | 0.97 (2) |
| O3—C5 | 1.3360 (17) | C6—C7 | 1.513 (2) |
| O3—C6 | 1.4641 (18) | C6—C8 | 1.510 (2) |
| N—C2 | 1.4457 (18) | C7—H7A | 0.980 |
| N—C3 | 1.4695 (19) | C7—H7B | 0.980 |
| N—C5 | 1.3478 (19) | C7—H7C | 0.980 |
| C1—C2 | 1.546 (2) | C8—H8A | 0.980 |
| C1—C4 | 1.517 (2) | C8—H8B | 0.980 |
| C2—H2 | 1.000 | C8—H8C | 0.980 |
| C3—H3A | 0.990 | | |
| H1O—O1—C2 | 106.6 (19) | C1—C4—H4B | 111.3 |
| C5—O3—C6 | 117.15 (11) | C3—C4—H4A | 111.3 |
| C2—N—C3 | 114.36 (12) | C3—C4—H4B | 111.3 |
| C2—N—C5 | 121.99 (12) | H4A—C4—H4B | 109.2 |
| C3—N—C5 | 123.58 (12) | O2—C5—O3 | 124.43 (13) |
| Br1—C1—Br2 | 108.05 (7) | O2—C5—N | 124.50 (13) |
| Br1—C1—C2 | 107.27 (9) | O3—C5—N | 111.06 (12) |
| Br1—C1—C4 | 110.95 (9) | O3—C6—H6 | 107.0 (13) |
| Br2—C1—C2 | 113.74 (9) | O3—C6—C7 | 105.83 (12) |
| Br2—C1—C4 | 112.98 (10) | O3—C6—C8 | 109.23 (12) |

| | | | |
|---|---|---|---|
| C2—C1—C4 | 103.71 (12) | H6—C6—C7 | 111.1 (13) |
| O1—C2—N | 110.45 (12) | H6—C6—C8 | 110.8 (13) |
| O1—C2—C1 | 111.97 (11) | C7—C6—C8 | 112.58 (13) |
| O1—C2—H2 | 111.3 | C6—C7—H7A | 109.5 |
| N—C2—C1 | 99.99 (11) | C6—C7—H7B | 109.5 |
| N—C2—H2 | 111.3 | C6—C7—H7C | 109.5 |
| C1—C2—H2 | 111.3 | H7A—C7—H7B | 109.5 |
| N—C3—H3A | 111.3 | H7A—C7—H7C | 109.5 |
| N—C3—H3B | 111.3 | H7B—C7—H7C | 109.5 |
| N—C3—C4 | 102.54 (11) | C6—C8—H8A | 109.5 |
| H3A—C3—H3B | 109.2 | C6—C8—H8B | 109.5 |
| H3A—C3—C4 | 111.3 | C6—C8—H8C | 109.5 |
| H3B—C3—C4 | 111.3 | H8A—C8—H8B | 109.5 |
| C1—C4—C3 | 102.32 (11) | H8A—C8—H8C | 109.5 |
| C1—C4—H4A | 111.3 | H8B—C8—H8C | 109.5 |

| | | | |
|---|---|---|---|
| C3—N—C2—O1 | 99.81 (14) | Br1—C1—C4—C3 | 73.49 (12) |
| C3—N—C2—C1 | −18.30 (15) | Br2—C1—C4—C3 | −165.00 (10) |
| C5—N—C2—O1 | −77.31 (17) | C2—C1—C4—C3 | −41.39 (13) |
| C5—N—C2—C1 | 164.59 (13) | N—C3—C4—C1 | 29.33 (14) |
| Br1—C1—C2—O1 | 161.81 (9) | C6—O3—C5—O2 | 5.0 (2) |
| Br1—C1—C2—N | −81.21 (11) | C6—O3—C5—N | −176.05 (12) |
| Br2—C1—C2—O1 | 42.39 (14) | C2—N—C5—O2 | 0.1 (2) |
| Br2—C1—C2—N | 159.37 (9) | C2—N—C5—O3 | −178.85 (12) |
| C4—C1—C2—O1 | −80.72 (13) | C3—N—C5—O2 | −176.76 (14) |
| C4—C1—C2—N | 36.26 (13) | C3—N—C5—O3 | 4.3 (2) |
| C2—N—C3—C4 | −6.68 (16) | C5—O3—C6—C7 | 152.87 (13) |
| C5—N—C3—C4 | 170.38 (13) | C5—O3—C6—C8 | −85.69 (15) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1O···O2$^{i}$ | 0.83 (3) | 1.92 (3) | 2.7479 (16) | 176 (3) |

Symmetry codes: (i) −*x*+1, −*y*, −*z*.

**Fig. 1**

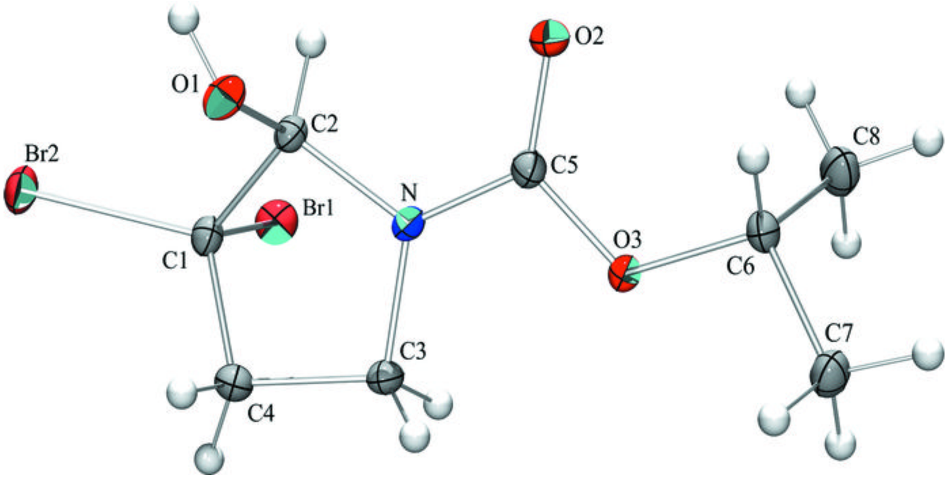

**Fig. 2**