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(2*R*,5*S*)-2-Trichloromethyl-3-oxa-1-azabicyclo-[3.3.0]octane-4,8-dione

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Key indicators

Single-crystal X-ray study
T = 190 K
Mean σ(C–C) = 0.002 Å
R factor = 0.027
wR factor = 0.064
Data-to-parameter ratio = 21.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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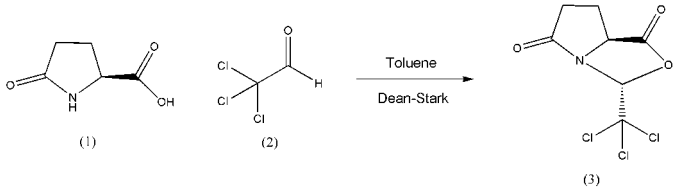
The crystal structure of the title bicyclic oxazolidindione, $C_7H_6Cl_3NO_3$, confirmed the absolute stereochemistry as 2*R*,5*S*.

Comment

Natural α-amino acids are at the core of many natural products (Ikota, 1992). (*S*)-pyroglutamic acid, in particular, forms the core of many excitatory amino acids, such as kaitocephalin (Watanabe *et al.*, 2002) and kainic acid (Oppolzer & Thirring, 1982). Synthetic routes to these classes of compounds require stereochemical control at various positions around a pyrrolidine ring. Seebach's method of the so-called self-reproduction of chirality involves a dual protection of the amine and carboxylic acid of (*S*)-proline with pivaldehyde to give a bicyclic system (Seebach *et al.*, 1983). The analogous protection of (*S*)-pyroglutamic acid was found to be unfavourable for pivaldehyde, the resulting product being particularly unstable (Dikshit *et al.*, 1995). However, analogous protection of (*S*)-pyroglutamic acid with chloral (Amedjkouh & Ahlberg, 2002) provided the title compound, (3) (shown in Fig. 1 and Table 1), as an air-stable crystalline solid.



(1) (2) (3)

Experimental

The title compound was prepared by the method described by Amedjkouh & Ahlberg (2002). Slow recrystallization from ethyl acetate gave colourless needle-like crystals. These tend to fracture when cut and therefore a large crystal was used. The multi-scan technique was used to correct for changes in the illuminated volume.

Crystal data

$C_7H_6Cl_3NO_3$
M_r = 258.49
Orthorhombic, $P2_12_12_1$
a = 6.0480 (1) Å
b = 10.1735 (3) Å
c = 15.5791 (4) Å
V = 958.57 (4) Å^3
Z = 4
D_x = 1.791 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 1485 reflections
θ = 5–30°
μ = 0.93 mm^{-1}
T = 190 K
Needle, colourless
0.80 × 0.20 × 0.20 mm

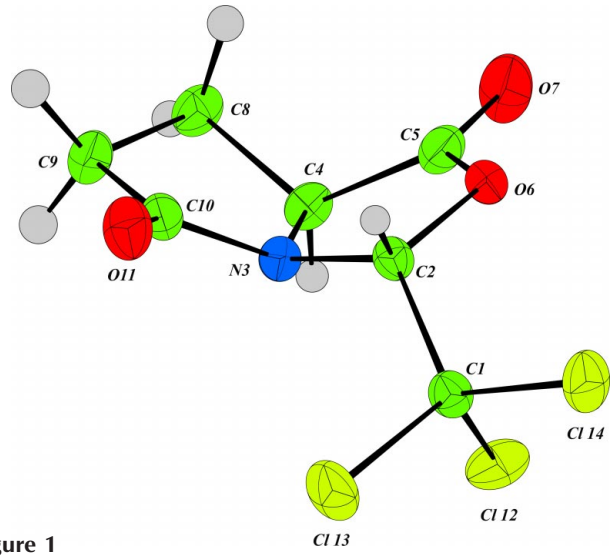


Figure 1
The molecular structure of (3), with displacement ellipsoids drawn at the 50% probability level. H-atom radii are arbitrary. Cl atoms are displayed in bright green.

Data collection

Nonius KappaCCD diffractometer	R_{int} = 0.028
ω scans	θ_{max} = 30.0°
Absorption correction: none	$h = -8 \rightarrow 8$
2708 measured reflections	$k = -14 \rightarrow 14$
2692 independent reflections	$l = -21 \rightarrow 21$
2545 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F^2) + 0.02 + 0.49p]$ where $p = [\max(F_o^2,0) + 2F_c^2]/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.027	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.064	$\Delta\rho_{max}$ = 0.27 e Å^{-3}
S = 0.95	$\Delta\rho_{min}$ = −0.26 e Å^{-3}
2692 reflections	Absolute structure: Flack (1983), 1104 Friedel pairs
128 parameters	Flack parameter = 0.01 (6)
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.544 (2)	C4—C5	1.516 (2)
C1—Cl12	1.7638 (16)	C4—C8	1.547 (2)
C1—Cl13	1.7617 (17)	C5—O6	1.366 (2)
C1—Cl14	1.7716 (16)	C5—O7	1.191 (2)
C2—N3	1.4352 (19)	C8—C9	1.531 (3)
C2—O6	1.4314 (19)	C9—C10	1.514 (3)
N3—C4	1.457 (2)	C10—O11	1.207 (2)
N3—C10	1.391 (2)		
C2—C1—Cl12	110.98 (10)	N3—C4—C5	102.17 (14)
C2—C1—Cl13	108.10 (11)	N3—C4—C8	105.25 (13)
Cl12—C1—Cl13	110.16 (9)	C5—C4—C8	117.03 (14)
C2—C1—Cl14	108.76 (11)	C4—C5—O6	109.41 (14)
Cl12—C1—Cl14	109.83 (9)	C4—C5—O7	129.11 (18)
Cl13—C1—Cl14	108.97 (8)	O6—C5—O7	121.44 (16)
C1—C2—N3	113.21 (12)	C2—O6—C5	110.71 (12)
C1—C2—O6	108.34 (12)	C4—C8—C9	102.61 (13)
N3—C2—O6	105.82 (11)	C8—C9—C10	104.36 (14)
C2—N3—C4	110.58 (12)	C9—C10—N3	106.57 (14)
C2—N3—C10	121.30 (13)	C9—C10—O11	129.32 (16)
C4—N3—C10	112.34 (13)	N3—C10—O11	124.11 (16)

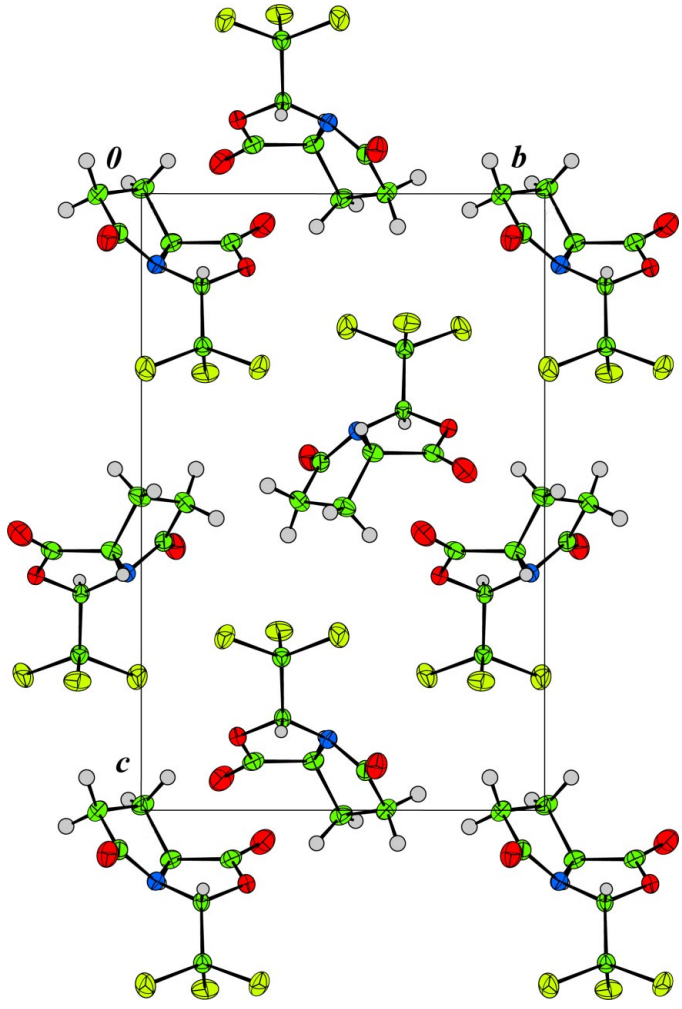


Figure 2
Packing diagram of (3), viewed down the *a* axis.

The H atoms were all seen in a difference map but those attached to C atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bonds to regularize their geometry [bond lengths to accepted values, angles either set by symmetry or to accepted values, and U_{iso}(H) dependent on the adjacent bonded atom], after which they were refined with riding constraints only. C—H = 0.93–0.98 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *COLLECT* (Nonius, 1997–2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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supporting information

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$b = 10.1735$ (3) Å
$c = 15.5791$ (4) Å
$V = 958.57$ (4) Å^3
$Z = 4$
$F(000) = 520$
$D_x = 1.791$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1485 reflections
$\theta = 5$–30°
$\mu = 0.93$ mm^{-1}
$T = 190$ K
Needle, colourless
0.80 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
Graphite monochromator
ω scans
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)
$T_{min} = 0.83$, $T_{max} = 0.83$
2708 measured reflections
2692 independent reflections
2545 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 30.0°$, $\theta_{min} = 5.2°$
$h = -8 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.064$
$S = 0.96$
2692 reflections
128 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\text{sigma}^2(F^2) + 0.02 + 0.49\text{p}]$ where $\text{p} = (\max(F_o^2,0) + 2F_c^2)/3$ Method = SHELXL 97 (Sheldrick, 1997)
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}
Absolute structure: Flack, (1983), 1104 Friedel-pairs
Absolute structure parameter: 0.01 (6)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.8490 (2)	0.15246 (16)	0.24808 (9)	0.0240
C2	0.8540 (2)	0.14921 (15)	0.14903 (9)	0.0205
N3	0.9665 (2)	0.03633 (13)	0.11515 (8)	0.0210

C4	1.1804 (3)	0.07368 (16)	0.07969 (10)	0.0247
C5	1.1657 (3)	0.22241 (17)	0.07900 (10)	0.0286
O6	0.9761 (2)	0.26093 (11)	0.11948 (7)	0.0252
O7	1.2939 (3)	0.30057 (14)	0.05136 (10)	0.0485
C8	1.1938 (3)	0.00394 (17)	−0.00842 (11)	0.0296
C9	1.0262 (3)	−0.10780 (18)	0.00128 (12)	0.0322
C10	0.8571 (3)	−0.05505 (15)	0.06413 (10)	0.0258
O11	0.6642 (2)	−0.08309 (13)	0.07187 (9)	0.0354
Cl12	1.11902 (7)	0.15831 (5)	0.29063 (3)	0.0363
Cl13	0.71158 (9)	0.01009 (4)	0.28416 (3)	0.0407
Cl14	0.69808 (8)	0.29265 (4)	0.28155 (3)	0.0352
H21	0.7008	0.1531	0.1278	0.0237*
H41	1.3021	0.0455	0.1181	0.0286*
H81	1.3388	−0.0319	−0.0172	0.0351*
H82	1.1486	0.0656	−0.0533	0.0354*
H91	1.1002	−0.1859	0.0264	0.0391*
H92	0.9571	−0.1357	−0.0533	0.0390*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0243 (7)	0.0219 (7)	0.0259 (6)	0.0005 (7)	0.0032 (5)	0.0002 (6)
C2	0.0194 (6)	0.0182 (6)	0.0240 (6)	0.0008 (6)	−0.0022 (5)	0.0006 (6)
N3	0.0192 (6)	0.0211 (6)	0.0227 (6)	0.0007 (5)	−0.0001 (5)	−0.0013 (5)
C4	0.0212 (7)	0.0296 (8)	0.0233 (7)	0.0000 (6)	0.0009 (6)	−0.0030 (6)
C5	0.0334 (9)	0.0304 (8)	0.0219 (7)	−0.0084 (7)	0.0034 (6)	−0.0047 (6)
O6	0.0324 (6)	0.0197 (5)	0.0235 (5)	−0.0020 (5)	0.0008 (5)	0.0012 (4)
O7	0.0617 (10)	0.0415 (7)	0.0423 (7)	−0.0242 (7)	0.0251 (7)	−0.0099 (6)
C8	0.0294 (8)	0.0336 (8)	0.0257 (7)	0.0051 (7)	0.0026 (6)	−0.0059 (6)
C9	0.0408 (10)	0.0271 (8)	0.0286 (8)	0.0018 (7)	−0.0021 (7)	−0.0071 (6)
C10	0.0301 (8)	0.0200 (7)	0.0272 (7)	−0.0006 (6)	−0.0058 (6)	0.0000 (6)
O11	0.0297 (6)	0.0305 (6)	0.0458 (7)	−0.0069 (5)	−0.0053 (5)	−0.0043 (5)
Cl12	0.03185 (19)	0.0504 (2)	0.02677 (17)	0.0041 (2)	−0.00816 (15)	−0.0008 (2)
Cl13	0.0530 (3)	0.02717 (19)	0.0420 (2)	−0.00685 (19)	0.0198 (2)	0.00310 (18)
Cl14	0.0385 (2)	0.02754 (19)	0.0396 (2)	0.00699 (17)	0.00566 (19)	−0.00887 (17)

Geometric parameters (Å, º)

C1—C2	1.544 (2)	C4—H41	0.991
C1—Cl12	1.7638 (16)	C5—O6	1.366 (2)
C1—Cl13	1.7617 (17)	C5—O7	1.191 (2)
C1—Cl14	1.7716 (16)	C8—C9	1.531 (3)
C2—N3	1.4352 (19)	C8—H81	0.960
C2—O6	1.4314 (19)	C8—H82	0.978
C2—H21	0.985	C9—C10	1.514 (3)
N3—C4	1.457 (2)	C9—H91	0.993
N3—C10	1.391 (2)	C9—H92	0.989
C4—C5	1.516 (2)	C10—O11	1.207 (2)

C4—C8	1.547 (2)		
C2—C1—Cl12	110.98 (10)	C8—C4—H41	111.354
C2—C1—Cl13	108.10 (11)	C4—C5—O6	109.41 (14)
Cl12—C1—Cl13	110.16 (9)	C4—C5—O7	129.11 (18)
C2—C1—Cl14	108.76 (11)	O6—C5—O7	121.44 (16)
Cl12—C1—Cl14	109.83 (9)	C2—O6—C5	110.71 (12)
Cl13—C1—Cl14	108.97 (8)	C4—C8—C9	102.61 (13)
C1—C2—N3	113.21 (12)	C4—C8—H81	110.425
C1—C2—O6	108.34 (12)	C9—C8—H81	109.705
N3—C2—O6	105.82 (11)	C4—C8—H82	108.963
C1—C2—H21	108.457	C9—C8—H82	111.198
N3—C2—H21	110.761	H81—C8—H82	113.404
O6—C2—H21	110.199	C8—C9—C10	104.36 (14)
C2—N3—C4	110.58 (12)	C8—C9—H91	109.562
C2—N3—C10	121.30 (13)	C10—C9—H91	109.503
C4—N3—C10	112.34 (13)	C8—C9—H92	114.037
N3—C4—C5	102.17 (14)	C10—C9—H92	111.890
N3—C4—C8	105.25 (13)	H91—C9—H92	107.434
C5—C4—C8	117.03 (14)	C9—C10—N3	106.57 (14)
N3—C4—H41	110.794	C9—C10—O11	129.32 (16)
C5—C4—H41	109.699	N3—C10—O11	124.11 (16)