

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1244). Services for accessing these data are described at the back of the journal.

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Intermediates for the Convenient Synthesis of Bicyclic Aziridinocarbamates

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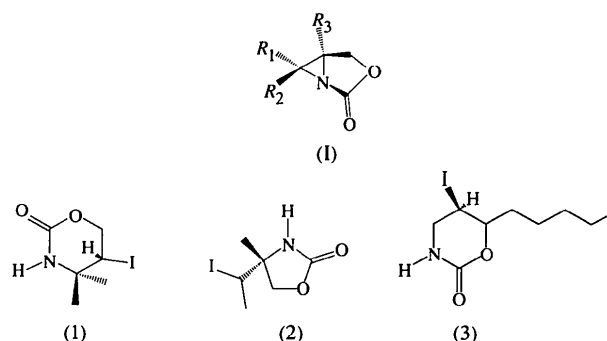
Abstract

3,4,5,6-Tetrahydro-5-iodo-4,4-dimethyl-2*H*-1,3-oxazin-2-one, C₆H₁₀INO₂, (1), 4,5-dihydro-4-(1-iodoethyl)-4-methyl-3*H*-1,3-oxazol-2-one, C₆H₁₀INO₂, (2), and 3,4,5,6-tetrahydro-5-iodo-6-(*n*-pentyl)-2*H*-1,3-oxazin-2-one, C₉H₁₆INO₂, (3), are examples of a series of readily prepared intermediates in a convenient synthesis of bi-

cyclic aziridinocarbamates. The structures obtained confirm the stereochemistries deduced from spectroscopic data. Compounds (1) and (2) exist in the solid state as centrosymmetric N—H···O hydrogen-bonded dimers: for (1), O1···N' = 2.901 (8), and for (2), N···O2' = 2.902 (4) Å. Compound (3) crystallizes with two independent molecules in the asymmetric unit which are hydrogen-bonded to form centrosymmetric tetramers: O2···N2' = 2.970 (6) and O4···N1' = 2.819 (6) Å.

Comment

Recently, a convenient synthesis of bicyclic aziridinocarbamates, (I), has been developed (Ensley & Ling, 1997) involving addition of iodine isocyanate to allylic alcohols. Despite the exclusive formation of the five-membered oxazolidinone ring in the final products, spectroscopic data on the cyclic iodide precursors to (I) suggested that some of these contained six-membered oxazinone rings. To confirm this, the structures of representative examples of these intermediates [(1)–(3)] were determined.



Compound (2) exists in the solid state as pairs of hydrogen-bonded molecules with N—H1*n*···O2' and N'—H1*n*'···O2 pairwise interactions: H1*n*···O2' = 2.03 (2) Å and N—H1*n*···O2' = 163 (1)° (primed atoms in the molecule at $-x, -y, -z$). Although the H atom bonded to N in (1) could not be located, it is likely that an analogous pairwise hydrogen bonding interaction occurs here as well based on the O1···N' distance of 2.901 (8) Å (primed atom in the molecule at $-1-x, 2-y, -z$) which is virtually identical to the N···O2' distance [2.902 (4) Å] seen in (2). In (3), hydrogen bonding occurs between the two independent molecules to give tetramers disposed about inversion centers (Fig. 4) with the aliphatic side chains disposed on the outer surfaces to generate hydrophobic channels between them. The hydrogen bonding involves O2—H2*n*'···N2' [O2···H2*n*' = 1.99 (2) Å and O2···H2*n*'—N2' = 166 (1)°; primed atoms in the molecule at $1-x, -y, 1-z$] and O4···H1*n*'—N1' [O4···H1*n*' = 1.98 (2) Å and O4···H1*n*'—N1' = 144 (1)°; primed

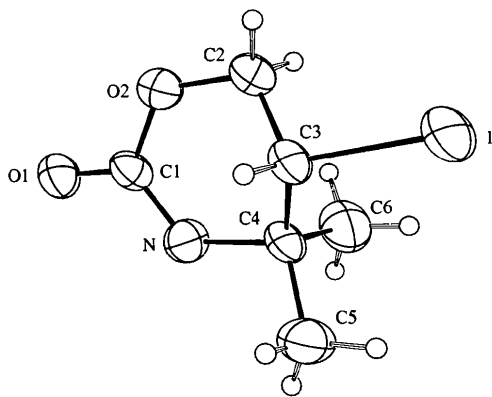


Fig. 1. ORTEP (Johnson, 1976) drawing of (1). Displacement ellipsoids are drawn at the 50% probability level except for H atoms which are drawn arbitrarily small.

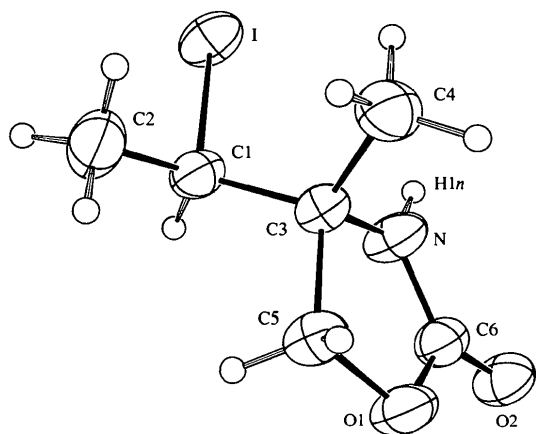


Fig. 2. ORTEP (Johnson, 1976) drawing of (2). Displacement ellipsoids are drawn at the 50% probability level except for H atoms which are drawn arbitrarily small.

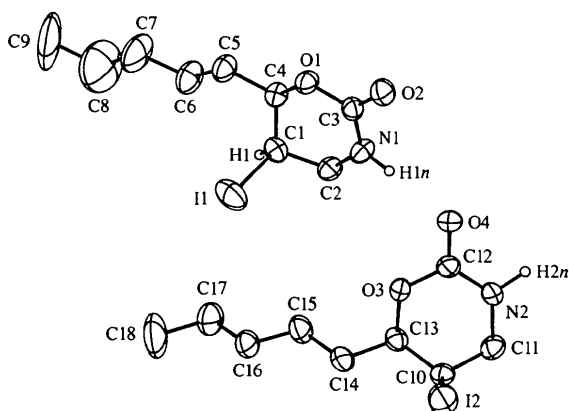


Fig. 3. ORTEP (Johnson, 1976) drawing of molecule A (top) and molecule B (bottom) in (3). Displacement ellipsoids are drawn at the 40% probability level except for H-atoms which are drawn arbitrarily small.

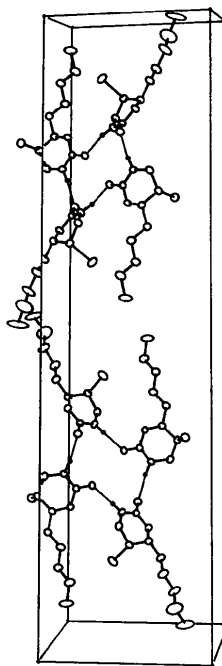


Fig. 4. Partial unit-cell contents of (3) showing the hydrogen bonding. The longest axis is the *a* axis and the *c* axis is out of the page.

atoms in the molecule at $-\frac{1}{2} + x, -\frac{1}{2} + y, z$. All distances and angles in the three molecules appear to be unexceptional and compare favorably with those found in related species (Friesen, Kolaczewska & Lough, 1992; Robinson, Hua, Good, Wang & Meyers, 1993; Turley, 1972; Stankovic *et al.*, 1985; Argay, Kalman, Kapor, Stajer & Bernath, 1985; Hirayama, Kohno, Shimizu & Kasai, 1991). The only significant difference between the two independent molecules, A and B, in (3) is the orientation of the aliphatic side chain, as is evident from Fig. 3, and the torsion angles C1—C4—C5—C6 [$-54.7(7)^\circ$] and C10—C13—C14—C15 [$-164.9(4)^\circ$]. For (1), the N, C1, C2, C4, O1, O2 portion is planar to within $0.020(7) \text{ \AA}$, with C3 $0.688(7) \text{ \AA}$ out of the plane, while in (3), only the N1, O1, O2, C2, C3 portion in A (N2, O3, O4, C11, C12 in B) is planar. The maximum deviation from the plane is $0.013(5) \text{ \AA}$ in A and $0.033(5) \text{ \AA}$ in B. In A, C1 and C4 are $0.491(5)$ and $-0.181(5) \text{ \AA}$, respectively, from the mean plane. Corresponding displacements in B are $0.551(5)$ and $-0.178(5) \text{ \AA}$, respectively, for C10 and C13. The O1, O2, C6, N, C5 portion of (2) is planar to within $0.016(5) \text{ \AA}$, with C3 $0.141(3) \text{ \AA}$ from the plane.

Experimental

Compounds (1)–(3), prepared as described elsewhere (Ensley & Ling, 1997), were recrystallized from chloroform/hexane

mixtures. Suitable crystals were cut to size and mounted on thin glass fibers with epoxy cement.

Compound (1)*Crystal data*C₆H₁₀INO₂M_r = 255.06

Triclinic

P1̄

a = 6.686 (3) Å

b = 11.304 (9) Å

c = 6.399 (2) Å

α = 95.46 (4)°

β = 113.56 (3)°

γ = 83.54 (5)°

V = 439.8 (4) Å³

Z = 2

D_x = 1.93 Mg m⁻³D_m not measured*Data collection*Enraf-Nonius CAD-4
diffractometer

θ/2θ scans

Absorption correction:

ψ scans (North, Phillips
& Mathews, 1968)T_{min} = 0.515, T_{max} = 0.630

1678 measured reflections

1535 independent reflections

Refinement

Refinement on F

R = 0.064

wR = 0.082

S = 2.216

1264 reflections

91 parameters

H atoms not refined

w = 4F_o²/[σ²(F_o²)
+ 0.0036F_o⁴]

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 23
reflections

θ = 13–16°

μ = 3.59 mm⁻¹

T = 293 K

Plate

0.43 × 0.33 × 0.13 mm

Colorless

1264 reflections with
I > 2σ(I)R_{int} = 0.031θ_{max} = 25°

h = 0 → 7

k = -13 → 13

l = -7 → 6

2 standard reflections

frequency: 120 min

intensity decay: -8.6%

(Δ/σ)_{max} = 0.002Δρ_{max} = 3.3 e Å⁻³Δρ_{min} = -2.1 e Å⁻³

Extinction correction: none

Scattering factors from *Inter-*
*national Tables for X-ray**Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °) for (1)

O1—C1	1.20 (1)	N—C1	1.341 (9)
O2—C1	1.354 (9)	N—C4	1.488 (9)
O2—C2	1.43 (1)		
C1—O2—C2	121.0 (6)	O2—C1—N	119.1 (7)
C1—N—C4	126.3 (6)	O2—C2—C3	111.3 (6)
O1—C1—O2	118.2 (7)	N—C4—C3	103.4 (6)
O1—C1—N	122.7 (7)		
C2—O2—C1—O1	178.6 (6)	C4—N—C1—O2	-3 (1)
C2—O2—C1—N	-0.2 (9)	C1—N—C4—C3	31.0 (9)
C1—O2—C2—C3	-27.4 (8)	C2—C3—C4—N	-55.6 (7)
C4—N—C1—O1	178.3 (5)		

Compound (2)*Crystal data*C₆H₁₀INO₂M_r = 255.06

Mo Kα radiation

λ = 0.71073 Å

Triclinic

P1̄

a = 6.1650 (9) Å

b = 6.762 (1) Å

c = 11.761 (1) Å

α = 102.81 (1)°

β = 90.09 (1)°

γ = 117.05 (1)°

V = 422.8 (1) Å³

Z = 2

D_x = 2.00 Mg m⁻³D_m not measured*Data collection*Enraf-Nonius CAD-4
diffractometer

θ/2θ scans

Absorption correction:

ψ scans (North, Phillips
& Mathews, 1968)T_{min} = 0.315, T_{max} = 0.619

1829 measured reflections

1664 independent reflections

Refinement

Refinement on F

R = 0.025

wR = 0.037

S = 1.39

1487 reflections

91 parameters

H atoms not refined

w = 4F_o²/[σ²(F_o²)
+ 0.0016F_o⁴]Cell parameters from 25
reflections

θ = 12–19°

μ = 3.73 mm⁻¹

T = 293 K

Plate

0.46 × 0.33 × 0.13 mm

Colorless

1487 reflections with
I > 3σ(I)R_{int} = 0.016θ_{max} = 25.97°

h = 0 → 7

k = -8 → 7

l = -14 → 14

2 standard reflections

frequency: 120 min

intensity decay: -2.2%

(Δ/σ)_{max} = 0.025Δρ_{max} = 0.79 e Å⁻³Δρ_{min} = -0.94 e Å⁻³

Extinction correction: none

Scattering factors from *Inter-*
*national Tables for X-ray**Crystallography* (Vol. IV)

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

O1—C5	1.430 (4)	N—C6	1.343 (4)
O1—C6	1.355 (4)	N—H1 _n	0.90 (2)
O2—C6	1.207 (4)	C3—C5	1.554 (4)
N—C3	1.455 (4)		
C5—O1—C6	109.5 (3)	O1—C5—C3	106.8 (3)
C3—N—C6	113.9 (3)	O1—C6—O2	121.8 (3)
C3—N—H1 _n	126 (1)	O1—C6—N	109.8 (3)
C6—N—H1 _n	120 (1)	O2—C6—N	128.4 (3)
N—C3—C5	99.0 (3)		
C6—O1—C5—C3	-7.2 (3)	C6—N—C3—C5	-8.9 (3)
C5—O1—C6—O2	-178.5 (3)	N—C3—C5—O1	9.3 (3)
C5—O1—C6—N	1.6 (4)		

Compound (3)*Crystal data*C₉H₁₆INO₂M_r = 297.14

Monoclinic

C2/c

a = 42.768 (9) Å

b = 11.338 (2) Å

c = 10.123 (1) Å

β = 102.16 (1)°

V = 4799 (1) Å³

Z = 16

D_x = 1.64 Mg m⁻³D_m not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25
reflections

θ = 12–17°

μ = 2.64 mm⁻¹

T = 293 K

Plate

0.43 × 0.36 × 0.20 mm

Colorless

Data collection

Enraf–Nonius CAD-4
diffractometer
 $\theta/2\theta$ scans
Absorption correction:
 ψ scans (North, Phillips
& Mathews, 1968)
 $T_{\min} = 0.332$, $T_{\max} = 0.593$
4511 measured reflections
4210 independent reflections

2840 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 25^\circ$
 $h = 0 \rightarrow 50$
 $k = 0 \rightarrow 13$
 $l = -12 \rightarrow 11$
2 standard reflections
frequency: 120 min
intensity decay: -9.9%

Refinement

Refinement on F^2
 $R = 0.039$
 $wR = 0.050$
 $S = 1.86$
2840 reflections
235 parameters
H atoms not refined
 $w = 4F_o^2 / [\sigma^2(F_o^2) + 0.0009F_o^4]$

$(\Delta/\sigma)_{\text{max}} = 0.039$
 $\Delta\rho_{\text{max}} = 0.74 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.17 \text{ e } \text{\AA}^{-3}$
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. Selected geometric parameters (\AA , $^\circ$) for (3)

O1—C3	1.340 (6)	O3—C12	1.362 (6)
O1—C4	1.466 (6)	O3—C13	1.455 (6)
O2—C3	1.212 (6)	O4—C12	1.212 (6)
N1—C2	1.440 (7)	N2—C11	1.457 (7)
N1—C3	1.341 (6)	N2—C12	1.337 (6)
N1—H1n	0.96 (4)	N2—H2n	1.00 (4)
C1—C2	1.503 (7)	C10—C11	1.510 (8)
C1—C4	1.490 (7)	C10—C13	1.514 (8)
C3—O1—C4	121.0 (4)	C12—O3—C13	120.5 (4)
C2—N1—C3	126.2 (4)	C11—N2—C12	126.0 (4)
C2—N1—H1n	127 (1)	C11—N2—H2n	124 (1)
C3—N1—H1n	105 (1)	C12—N2—H2n	110 (1)
C2—C1—C4	109.1 (4)	C11—C10—C13	108.4 (4)
N1—C2—C1	110.7 (4)	N2—C11—C10	110.7 (4)
O1—C3—O2	117.5 (5)	O3—C12—O4	118.0 (5)
O1—C3—N1	117.8 (5)	O3—C12—N2	118.2 (4)
O2—C3—N1	124.7 (5)	O4—C12—N2	123.8 (5)
O1—C4—C1	111.1 (4)	O3—C13—C10	110.7 (4)
O1—C4—C5	105.3 (4)	O3—C13—C14	106.6 (4)
C1—C4—C5	117.6 (5)	C10—C13—C14	116.4 (5)
C4—O1—C3—O2	172.3 (4)	C13—O3—C12—O4	173.1 (4)
C4—O1—C3—N1	-10.1 (6)	C13—O3—C12—N2	-7.4 (6)
C3—O1—C4—C1	37.5 (6)	C12—O3—C13—C10	38.6 (6)
C3—O1—C4—C5	165.8 (4)	C12—O3—C13—C14	166.1 (4)
C3—N1—C2—C1	-22.2 (7)	C12—N2—C11—C10	-18.0 (7)
C2—N1—C3—O1	2.3 (7)	C11—N2—C12—O3	-3.6 (7)
C2—N1—C3—O2	179.8 (5)	C11—N2—C12—O4	175.9 (4)
C4—C1—C2—N1	46.8 (5)	C13—C10—C11—N2	46.6 (5)
C2—C1—C4—O1	-54.7 (5)	C11—C10—C13—O3	-57.1 (5)
C2—C1—C4—C5	-176.0 (4)	C11—C10—C13—C14	-179.0 (4)

General procedures for crystal orientation, unit-cell determination, and refinement and collection of intensity data have been published (Mague & Lloyd, 1989). For (1) and (2), no cells of higher symmetry than the initially determined triclinic ones could be found and, with reasonable densities calculated with $Z = 2$, $P\bar{1}$ was selected for the space groups. For (3), the observed systematic absences were consistent with either Cc or $C2/c$. As the intensity statistics indicated a centrosymmetric space group, the latter was chosen. In all three cases, the choice was confirmed by the successful refinement. Following location of the I atom(s) by the indicated methods, refinement proceeded satisfactorily and virtually all H atoms, except for

that attached to N in (1) and to the methyl groups in (3), could be seen in $\Delta\rho$ maps in the final stages. Those attached to C3 in (1), C1 and N in (2), and C1, C4, N1, C10, C13 and N2 in (3) were placed in the positions indicated by the $\Delta\rho$ maps and allowed to ride on the attached atoms. The remainder, except for the methyl H atoms of (3) for which no reliable positions could be found, were placed in calculated positions ($C-H = 0.98 \text{ \AA}$) and updated periodically. All H atoms were assigned isotropic displacement parameters 1.2 times those of the attached atoms. The major features in the $\Delta\rho$ map for (1) are all within 1.0 \AA of the I atom and presumably result from the combined results of crystal decomposition and shortcomings in the empirical absorption correction. The large anisotropic displacement parameters for C8, and particularly C9, in (3) suggested disorder for this portion of the *n*-pentyl substituent. However, careful inspection of $\Delta\rho$ maps in this region gave no indication of resolved alternate positions for these atoms. Consequently, only one site was refined for each.

For all compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structures: Patterson and Fourier methods for (1) and (2); direct methods using *MULTAN80* (Main *et al.*, 1980) for (3). For all compounds, program(s) used to refine structures: *LSFM* in *MolEN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *CIF VAX* in *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1050). Services for accessing these data are described at the back of the journal.

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