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Two isomers of 1,4a,5,7,8,9,9a,10,11,12a-decahydro-1,4-methanocyclopenta[*b*]pyrrolo[1,6a-*a*][3,1]benzoxazin-11-one

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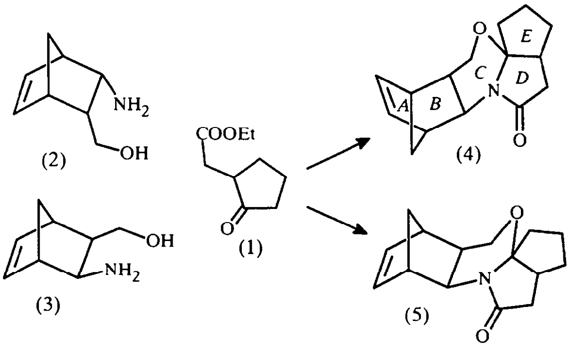
Abstract

The reactions of 2-ethoxycarbonylmethylcyclopentanone with *diendo*- or *diexo*-3-aminobicyclo[2.2.1]hept-5-ene-2-methanol yielded isomeric cyclopentan[*b*]pyrrolo[1,6a-*a*][3,1]benzoxazinones. The crystal structures of the two isomers ($C_{15}H_{19}NO_2$) were elucidated by means of X-ray crystallography.

Comment

2-Aroylcyclohexanecarboxylic acids were earlier used to prepare tetra- and pentacyclic compounds containing two hetero rings and one or two cycloalkane rings at the terminal(s), with isoindolone or indolone as the central structural unit (Stájer *et al.*, 1994, 1996; Sillanpää *et al.*, 1997; Virág *et al.* 1998). The aim of these syntheses was to obtain pharmacologically active compounds. The preparation of the saturated derivatives yielded isomeric compounds with different stereostructures. Similar reactions of β-oxocycloalkanecarboxylates afforded condensed-skeleton bicyclic lactams, thiophenes, pyrones *etc.* (Omar & Frahm, 1990; Noe *et al.*, 1986; Hua *et al.*, 1990; Kraatz, 1984).

The above reactions have now been extended to those between 2-ethoxycarbonylmethylcyclopentanone, (1), and *diendo*-, (2), and *diexo*-3-aminobicyclo[2.2.1]hept-5-ene-2-methanol, (3). Whereas the earlier applied γ-oxocarboxylic acids, such as 2-aroylcyclohexanecarboxylic acid, led to isoindolones, (1) yielded saturated norbornene and cyclopentane-condensed pyrrolones. The differences from the similar compounds where ring *A* was *cis*- or *trans*-fused cyclohexane or cyclohexene, and ring *E* either cyclopentane or cyclohexane (Virág *et al.*, 1998), are as follows: (*a*) ring *A* is methylene-bridged and fused *diendo* or *diexo* here, always containing a double bond, and (*b*) ring *E* is now a fused cyclopentane moiety.



Compound (1), prepared by a literature method (Mondon, 1959), was reacted with *diendo*-, (2), or *diexo*-3-aminobicyclo[2.2.1]hept-5-ene-2-methanol, (3) (Stájer *et al.*, 1983, 1984), to yield methanocyclopenta[*b*]pyrrolo[1,6a-*a*][3,1]benzoxazinones [(4) and (5)]. As (4) and (5) gave overlapping signals, the stereostructures could not be established by NMR methods. X-ray analysis, however, allowed elucidation of the structures. Perspective views of (4) and (5) are depicted in Figs. 1 and 2, respectively. The measurements prove the *cis* positions of the annulational H atoms on C4a, C12a and C9a (cyclopentane annulational H atom); thus, the O6—C6a and C9a—H bonds are in the same steric orientation in both cases. Furthermore, for (5), the bridging methylene is close to the oxazine O atom; hence, the olefinic H atoms are far from the latter. Structure (4) contains the olefinic H atoms near to and the 13-methylene group far from this oxygen. The above steric character, *i.e.* the identical steric orientation of the heterocyclic-O atom and the annulational H atom, is characteristic for analogous compounds which contain a cyclohexane or cyclohexene ring *D* (Sillanpää *et al.*, 1997; Virág *et al.*, 1998). At the same time, structures (4) and (5) confirm our earlier finding that the reacting cyclic or bicyclic amino alcohols retain their starting configuration in almost every case.

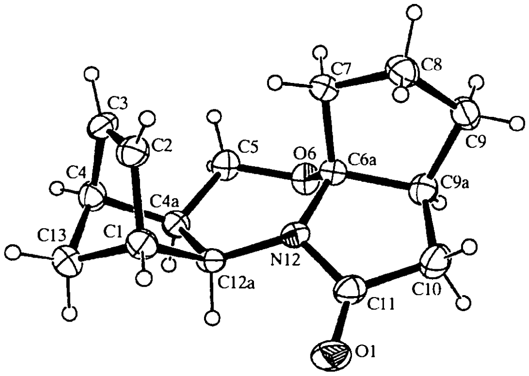


Fig. 1. *ORTEP*-3 (Farrugia, 1997) plot of (4). Only the heavy atoms have been labelled. Displacement ellipsoids are drawn at the 30% probability level.

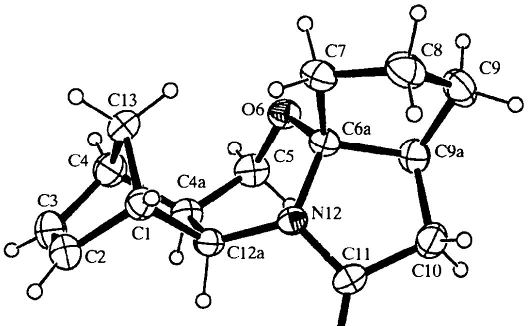


Fig. 2. *ORTEP*-3 (Farrugia, 1997) plot of (5). Only the heavy atoms have been labelled. Displacement ellipsoids are drawn at the 30% probability level.

The bonding parameters in both compounds are normal (Tables 1 and 2). In (4), the conformation of ring *C* is quite different compared to that in (5). For (4), the torsion-angle values (Table 1) suggest a distorted sofa conformation for ring *C* while the values for (5) indicate a twist-boat form. The dramatic difference reflects the tendency of lone electron pairs at the O and N atoms to avoid each other as much as possible.

Experimental

A mixture of ethyl 2-oxocyclopentylacetate, (1) (1.70 g, 0.01 mol), *diendo*-, (2), and *diexo*-3-aminobicyclo[2.2.1]hept-5-ene-2-methanol, (3) (1.40 g, 0.01 mol), and *p*-toluenesulfonic acid (0.05 g) in dry toluene (40 cm^3) was refluxed for 8 h. After evaporation to dryness, the residue was purified on a silica-gel column (Acros, 0.035–0.07 mm) using an *n*-hexane–EtOAc (3:1) mixture as eluant. After evaporation of the solvent, the residue was crystallized from diethyl ether. Colourless crystals: (4) m.p. 395–397 K, yield 1.05 g (42.8%); (5) m.p. 339–341 K, yield 1.00 g (40.8%). Analysis calculated for $C_{15}H_{19}NO_2$: C 73.43, H 7.81, N 5.71%. Found: C 73.30, H 7.65, N 5.67% (4); C 73.55, H 7.80, N 5.70% (5).

Compound (4)

Crystal data

$C_{15}H_{19}NO_2$
$M_r = 245.31$
Triclinic
$P\bar{1}$
$a = 8.7236\,(18)$ Å
$b = 9.748\,(3)$ Å
$c = 8.1340\,(19)$ Å
$\alpha = 98.28\,(2)^\circ$
$\beta = 109.745\,(16)^\circ$
$\gamma = 100.48\,(2)^\circ$
$V = 624.2\,(3)$ Å^3
$Z = 2$
$D_x = 1.305$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 15.8$–18.2°
$\mu = 0.086$ mm^{-1}
$T = 294\,(2)$ K
Needle
0.36 × 0.34 × 0.20 mm
Colourless

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2363 measured reflections
2202 independent reflections
1558 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.018$
$\theta_{\rm max} = 25^\circ$
$h = 0 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -10 \rightarrow 10$
3 standard reflections every 150 reflections intensity decay: 0.58%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.106$
$S = 1.036$
2202 reflections
163 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 0.2245P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.166$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.148$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (4)*

O1—C11	1.224 (3)	N12—C6a	1.468 (2)
O6—C6a	1.421 (2)	N12—C12a	1.469 (2)
O6—C5	1.441 (2)	C2—C3	1.321 (3)
N12—C11	1.360 (3)		
C6a—O6—C5	111.35 (15)	O6—C6a—N12	108.74 (15)
C11—N12—C6a	113.81 (17)	O6—C6a—C7	112.87 (16)
C11—N12—C12a	118.75 (17)	N12—C6a—C7	114.22 (16)
C6a—N12—C12a	122.71 (15)	O6—C6a—C9a	110.22 (16)
C2—C1—C13	100.10 (18)	N12—C6a—C9a	104.71 (16)
C2—C1—C12a	108.97 (17)	O1—C11—N12	124.6 (2)
C13—C1—C12a	98.45 (17)	O1—C11—C10	126.3 (2)
C3—C2—C1	107.9 (2)	N12—C11—C10	109.03 (19)
C2—C3—C4	107.5 (2)	N12—C12a—C1	118.04 (17)
O6—C5—C4a	111.91 (16)	N12—C12a—C4a	114.41 (16)
C6a—O6—C5—C4a	−64.5 (2)	C12a—N12—C6a—O6	−37.4 (2)
C12a—C4a—C5—O6	33.2 (2)	C6a—N12—C12a—C4a	9.7 (3)
C5—O6—C6a—N12	64.7 (2)	C5—C4a—C12a—N12	−7.1 (2)

Compound (5)

Crystal data

$C_{15}H_{19}NO_2$
$M_r = 245.31$
Monoclinic
$C2/c$
$a = 18.5108\ (18)$ Å
$b = 6.644\ (4)$ Å
$c = 21.2349\ (15)$ Å
$\beta = 105.690\ (6)°$
$V = 2514.4\ (16)$ Å^3
$Z = 8$
$D_x = 1.296$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 16.9–19.8°$
$\mu = 0.086$ mm^{-1}
$T = 294\ (2)$ K
Plate
0.36 × 0.34 × 0.22 mm
Colourless

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2508 measured reflections
2209 independent reflections
1530 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.007$

$\theta_{\rm max} = 25.01°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 8$
$l = -25 \rightarrow 25$
3 standard reflections every 150 reflections intensity decay: 0.55%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.118$
$S = 1.026$
2209 reflections
163 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 1.624P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.155$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.175$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (5)*

O1—C11	1.228 (2)	N12—C12a	1.453 (2)
O6—C6a	1.431 (2)	N12—C6a	1.458 (2)
O6—C5	1.431 (3)	C2—C3	1.314 (4)
N12—C11	1.365 (2)		
C6a—O6—C5	114.13 (15)	O6—C6a—N12	109.74 (15)
C11—N12—C12a	121.05 (16)	O6—C6a—C7	107.07 (16)
C11—N12—C6a	114.29 (16)	N12—C6a—C7	115.18 (16)
C12a—N12—C6a	122.78 (15)	O6—C6a—C9a	115.33 (17)
C2—C1—C13	99.14 (18)	N12—C6a—C9a	104.25 (16)
C2—C1—C12a	103.45 (18)	O1—C11—N12	125.05 (19)
C13—C1—C12a	102.74 (17)	O1—C11—C10	126.25 (18)
C3—C2—C1	107.9 (2)	N12—C11—C10	108.70 (18)
C2—C3—C4	107.9 (2)	N12—C12a—C1	117.68 (17)
C5—C4a—C4	117.86 (19)	N12—C12a—C4a	109.93 (16)
O6—C5—C4a	112.49 (18)		
C6a—O6—C5—C4a	65.8 (2)	C12a—N12—C6a—O6	−33.6 (2)
C12a—C4a—C5—O6	−47.5 (2)	C6a—N12—C12a—C4a	47.3 (2)
C5—O6—C6a—N12	−24.2 (2)	C5—C4a—C12a—N12	−4.2 (2)

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1995); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1062). Services for accessing these data are described at the back of the journal.

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