H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0924P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from
International Tables for
Crystallography (Vol. C)

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

Br1—C2	1.890 (7)	C4—N2	1.455 (12)
C1—N1	1.349 (12)	N1···O1″	2.941 (9)
C1—C2′	1.404 (8)	N1···O1‴	2.941 (9)
C1—C2	1.404 (8)	N2—O1′	1.234 (6)
C2—C3	1.384 (10)	N2—O1	1.234 (6)
C3—C4	1.388 (8)	O1···H1A⁗	2.334 (9)
C4—C3′	1.388 (8)	O1···Br1ᵛ	3.218 (5)
N1—C1—C2′	121.6 (4)	C1—N1—O1″	157.9 (2)
N1—C1—C2	121.6 (4)	C1—N1—O1‴	157.9 (2)
C2′—C1—C2	116.9 (8)	O1″—N1—O1‴	43.1 (2)
C3—C2—C1	122.3 (6)	O1′—N2—O1	122.7 (8)
C3—C2—Br1	118.4 (5)	O1′—N2—C4	118.6 (4)
C1—C2—Br1	119.3 (5)	O1—N2—C4	118.6 (4)
C2—C3—C4	118.1 (6)	N2—O1···H1Aᵛ	110.6 (5)
C3′—C4—C3	122.2 (9)	N2—O1···Br1ᵛ	149.3 (5)
C3′—C4—N2	118.9 (5)	H1A⁗···O1···Br1ᵛ	97.5 (2)
C3—C4—N2	118.9 (5)		

Symmetry codes: (i) $x, \frac{3}{2} - y, z$; (ii) $x - 1, \frac{3}{2} - y, 1 + z$; (iii) $x - 1, y, 1 + z$; (iv) $1 + x, \frac{3}{2} - y, z - 1$; (v) $1 - x, 1 - y, -z$.

Unit-cell dimensions were determined from reflections taken from three sets of 30 frames (at 0.3° steps in ω), each at 20 s exposure. A full hemisphere of reciprocal space was scanned by 0.3° ω steps at φ = 0, 90 and 180°, with the area detector held at 2θ = −29°. The crystal-to-detector distance was 4.974 cm. Crystal decay was monitored by repeating the initial 50 frames at the end of data collection and analysing the duplicate reflections. No decay was observed. H atoms were constrained to idealized geometries; each was assigned an isotropic displacement parameter of 1.2 times the U_{eq} value of the attached aromatic C or amide N atom.

Data collection: *SMART* (Siemens, 1995a). Cell refinement: *SAINT* (Siemens, 1995a). Data reduction: *SAINT.* Program(s) used to solve structure: *SHELXTL* (Siemens, 1995b). Program(s) used to refine structure: *SHELXTL.* Molecular graphics: *SHELXTL.* Software used to prepare material for publication: *SHELXTL.*

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17β-Hydroxymethyl-3-methoxy-19,21-dinorestra-1,3,5(10)-trieno-18,20-lactone

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Abstract

An intramolecular oxygenation sequence leads to the hitherto unknown C-17,C-18-bridged title estrane derivative, $C_{20}H_{24}O_3$. The requisite assignment of its configuration was carried out by X-ray analysis.

Comment

For the synthesis of norestradiol (Kuhl *et al.*, 1997), we investigated one route *via* functionalization of the angular C-18 methyl group of alcohol (1) (Kuhl & Kreiser, 1998; Precigoux *et al.*, 1980) by an intramolecular radical-mediated oxygenation known as the hypoiodite reaction (Kalvoda & Heusler, 1971). The structure of the previously unknown title lactone (2) displays some outstanding features of estrane derivatives with an aromatic *A* ring. In contrast to the usual case, where the *B* ring adopts a significantly distorted half-chair or deformed sofa conformation (Geise *et al.*, 1967), compound (2)

(1)   (2)
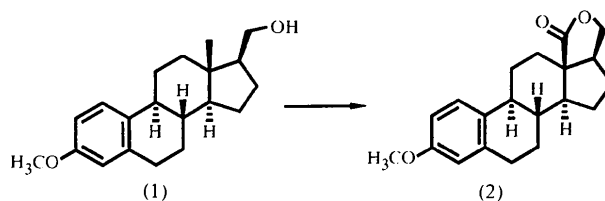
approximates an ideal half-chair, indicated by the torsion angle C7—C8—C9—C10 of 50.6 (3)°. As a result of this, the *C* ring possesses an undistorted chair conformation, verified by the mean of the absolute values of the corresponding torsion angles of 55 (1)° (Kutschabsky *et al.*, 1985). In contrast, the *D* ring displays a dramatically deformed C14α-envelope conformation ($\Delta = -17.9$ and $\varphi_m = 34.4°$) in terms of puckering (Altona

et al., 1968). In our opinion, these structural features are due to the conformational transmission effect from the *E* ring, which abides in a 17β-envelope form (Δ = −34.8 and φ_m = 31.9°). Atoms C13, C18, O2 and C20 form a plane, with a maximum deviation of 0.025 Å from planarity, nearly perpendicular to the *D* ring; the torsion angle C18—C13—C17—C16 is 88.8 (3)°. The conformation shown in Fig. 1 is the absolute one since the starting material was derived from enantiomerically pure estrol (1) (Kuhl & Kreiser, 1998) with known absolute configuration.
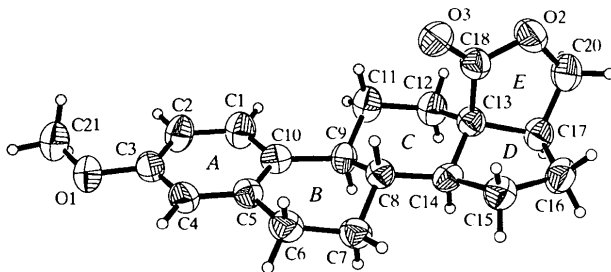

Fig. 1. View of the title compound (*SHELXTL-Plus*; Sheldrick, 1991) showing the labelling of all non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as circles of arbitrary radii.

Experimental

The hypoiodite reaction was performed with 1.3 equivalents of iodine and 3.4 equivalents of thoroughly powdered Pb(OAc)$_4$ in cyclohexane under reflux, using dry CaCO$_3$ as a buffer (Meystre *et al.*, 1962). Subsequent displacement of iodine by treatment with sodium acetate in a solution of acetic acid under reflux and oxidation with the CrO$_3$–pyridine complex (Poos *et al.*, 1953) provided, after agitation with diethyl ether and one crystallization from ethyl acetate, pure lactone (2) (m.p. 464–465 K) in 15% overall yield.

Crystal data

$C_{20}H_{24}O_3$	Mo $K\alpha$ radiation
$M_r = 312.39$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 15
$P2_1$	reflections
$a = 6.524\,(1)$ Å	$\theta = 10.0–17.5°$
$b = 7.412\,(1)$ Å	$\mu = 0.084$ mm^{-1}
$c = 16.875\,(3)$ Å	$T = 293\,(2)$ K
$\beta = 93.72\,(3)°$	Needle
$V = 814.3\,(2)$ Å^3	$0.58 \times 0.18 \times 0.12$ mm
$Z = 2$	Yellow
$D_x = 1.274$ Mg m^{-3}	
D_m not measured	

Data collection

Nonius Kappa-CCD diffractometer	1596 reflections with $I > 2\sigma(I)$

360 frames *via* ω rotation ($\Delta\omega$ = 1°) and two times 10 s per frame. Absorption correction: none. 5495 measured reflections. 2615 independent reflections.

$R_{int} = 0.030$
$\theta_{max} = 24.69°$
$h = -7 \rightarrow 7$
$k = -8 \rightarrow 8$
$l = -19 \rightarrow 19$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.112$
$S = 0.856$
2613 reflections
233 parameters
Only H-atom U's refined; H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 0.0056P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.037$
$\Delta\rho_{max} = 0.120$ e Å^{-3}
$\Delta\rho_{min} = -0.115$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.039 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected torsion angles* (°)

C7—C8—C9—C10	50.6 (3)	C18—C13—C17—C20	−30.4 (3)
C8—C9—C11—C12	54.2 (3)	C18—C13—C17—C16	88.8 (3)
C9—C11—C12—C13	−54.2 (4)	C14—C13—C17—C16	−31.0 (3)
C11—C12—C13—C14	54.0 (3)	C15—C16—C17—C13	7.9 (3)
C9—C8—C14—C13	55.8 (3)	C17—C13—C18—O2	20.2 (4)
C12—C13—C14—C8	−56.8 (3)	C13—C17—C20—O2	31.2 (4)
C17—C13—C14—C15	43.0 (3)	C13—C18—O2—C20	−1.0 (4)
C13—C14—C15—C16	−37.3 (3)	C17—C20—O2—C18	−19.4 (4)
C14—C15—C16—C17	18.1 (3)		

The data collection covered the whole sphere of reciprocal space. The crystal-to-detector distance was 2.6 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. The structure was solved by direct methods (Sheldrick, 1990) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (Sheldrick, 1997). H atoms were placed in calculated positions and refined with a riding model (including free rotation about O—C). *SHELXTL-Plus* (Sheldrick, 1991) was used to produce the ellipsoid plot.

Data collection: Nonius Kappa-CCD software. Cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997). Data reduction: *DENZO* and *SCALEPACK*. Software used to prepare material for publication: *SHELXL97* and *PARST95* (Nardelli, 1995).

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(9-Anthrylmethyl)bis(2-pyridylmethyl)amine

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Abstract

The title compound, $C_{27}H_{23}N_3$, crystallizes in space group $P2_1/c$. The anthryl groups of molecules related by a center of symmetry stack together forming dimers. These units pack in a herring-bone pattern in the (100) plane.

Comment

The title compound, (1), was prepared as part of our research on novel photo-induced electron-transfer (PET) sensors for protons and post transition metal ions. It behaves as an off–on–off fluorescent switch for protons, due to two independent PET processes which occur between the anthracene chromophore and the proton receptors (tertiary nitrogen and the pyridyl groups) at different pH values. The sensor (1) responds to zinc(II) ions as an off–on switch by using only one of these PET processes (de Silva *et al.*, 1997). Compound (1) has also been reported as a ligand in a cobalt(II) complex used for DNA cleavage (Bhattacharya & Mandal, 1996).

(1)
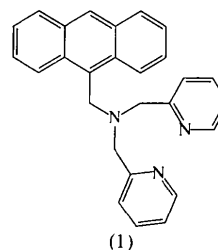
The numbering scheme and a displacement ellipsoid plot of (1) are shown in Fig. 1. Bond distances and angles are in agreement with related compounds containing a (1-naphthylmethyl)bis(2-pyridylmethyl)amine fragment (Bag *et al.*, 1995). The molecular structure consists of three nearly planar fragments connected to an amine N atom by methylene groups. The largest deviation from the mean plane of the anthryl group (C11–C16, C21–C24, C31–C34) is 0.022 (2) Å for C11, and the largest deviations from the mean planes through the pyridyl groups are 0.007 (3) Å for C45 and −0.007 (3) Å for C44. The dihedral angles between the anthryl group and the two pyridyl rings are 68.97 (9)° for the N40-containing ring and 66.16 (8)° for the N50-containing ring. The angle between the two pyridyl rings is 51.2 (1)°. A view of the packing in the crystal is shown in Fig. 2. The molecules pack as dimers about inversion centers with the anthryl groups stacked together. The separation of the best planes between centrosymmetrically related anthryl groups is 3.45 (1) Å (symmetry code: $-x$, $-y$, $2-z$). These units form a herringbone pattern in a layer about the (100) plane of the unit cell. The bis(N-pyridylmethyl)methyleneamine portions of the molecules jut out from each side of the layer interacting with the pyridyl rings from adjacent layers. The packing of anthryl groups in (1) resembles that of aromatic compounds such as pyrene. This pattern has
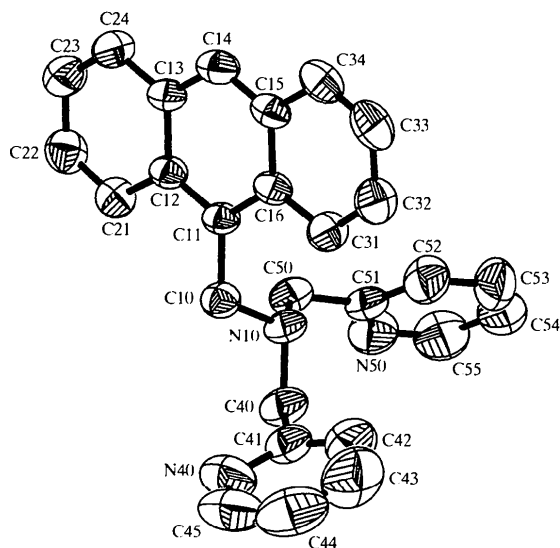

Fig. 1. The structure of (1) showing 50% probability displacement ellipsoids. The H atoms have been omitted for clarity.