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Acta Cryst. (1996). C**52**, 2037-2040

17α-Benzyl-17β-hydroxy-16-hydroxyimino-3-methoxyestra-1,3,5(10)-triene

Slobodanka Stanković,[a] Dušan Lazar,[a] Dušan Miljković,[b] Ljubica Medić-Mijačević,[b] Katarina Gaši,[b] Radmila Kovačević[c] and Christiane Courseille[d]

[a]*Institute of Physics, Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića 4, 21000 Novi Sad, Serbia,* [b]*Institute of Chemistry, Faculty of Sciences, University of Novi Sad, Novi Sad, Serbia,* [c]*Institute of Biology, Faculty of Sciences, University of Novi Sad, Novi Sad, Serbia, and* [d]*Laboratoire de Cristallographie et de Physique Cristalline, Faculté des Sciences, Université de Bordeaux I, Talance, France*

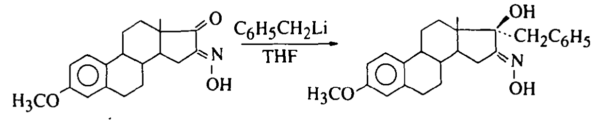
(*Received 1 May 1995; accepted 28 November 1995*)

Abstract

The asymmetric unit of the title compound, 17α-benzyl-16-hydroxyimino-3-methoxyestra-1,3,5(10)-trien-17β-ol, $C_{26}H_{31}NO_3$, contains two molecules which differ in the orientations of the methoxy groups at C(3). The 17-hydroxy and 16-hydroxyimino moieties are involved in intramolecular N···O and intermolecular N···O and O···O hydrogen bonds. The hydrogen-bond network accounts for the differences in bond and torsion angles of the α-hydroxyimino moieties of the symmetry-independent molecules. This has been confirmed by molecular-mechanics calculations on the individual molecules which indicate that they have the same geometry in their energy minimum states.

Comment

As a part of our study of the Beckmann fragmentation reaction in a series of steroidal tertiary α-hydroxyimino alcohols, the synthesis of 17α-benzyl-17β-hydroxy-16-hydroxyimino-3-methoxyestra-1,3,5(10)-triene, (2), was performed (Miljković, Gaši, Medić-Mijačević, Stanković & Lazar, 1995). Regioselective addition of benzyllithium to the 17-carbonyl group of 16-hydroxyimino-3-methoxyestra-1,3,5(1)-triene-17-one, (1), afforded the title compound, (2). Its structure, deduced from chemical spectroscopic evidence, was confirmed by X-ray diffraction analysis.



(1) (2)

Perspective views of the two symmetry-independent molecules, (I) and (II), of compound (2) are shown in Fig. 1. Selected geometric parameters are given in Table 2, together with corresponding values (in square brackets) obtained from molecular-mechanics calculations. The puckering (Cremer & Pople, 1975) and asymmetry parameters (Duax, Weeks & Rohrer, 1976) listed in Table 3 reveal usual ring conformations. Ring *B* has a 7α,8β-half-chair conformation; the distances of atoms C(7) and C(8) from the best plane of the remaining four atoms are −0.369 (7) and 0.413 (6) Å, respectively, for molecule (I), and −0.319 (7) and 0.437 (6) Å for molecule (II). Ring *C* has a chair conformation, while ring *D* exhibits a conformation between a 13β-envelope [the distance of atom C(13) from the best

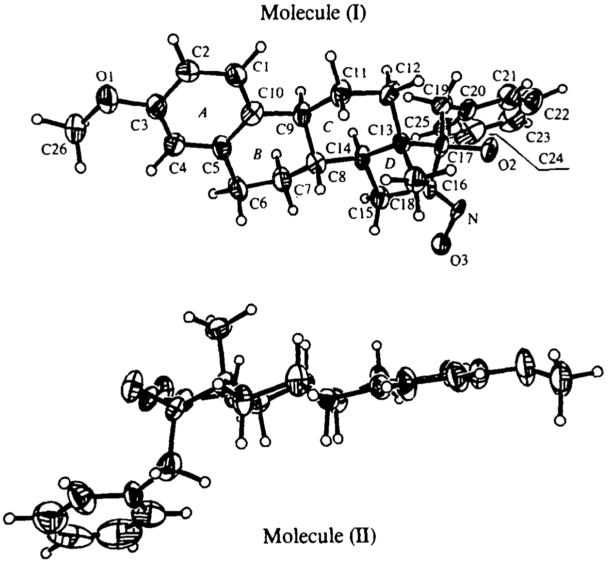


Fig. 1. A perspective view of the two symmetry-independent molecules, (I) and (II), of the title compound. Displacement ellipsoids are plotted at the 40% probability level.

plane of the remaining four atoms is 0.662 (5) Å for molecule (I) and 0.696 (6) Å for molecule (II)] and a 13β,14α-half-chair [the distances of atoms C(13) and C(14) are 0.551 (5) and −0.144 (6) Å for molecule (I), and 0.574 (6) and −0.159 (6) Å for molecule (II)]. The C(1)—C(10)···C(13)—C(18) non-bonded torsion angles [89.0 (7)° for (I) and 85.9 (8)° for (II)] show that there is no twist along the principal axis of either molecule.

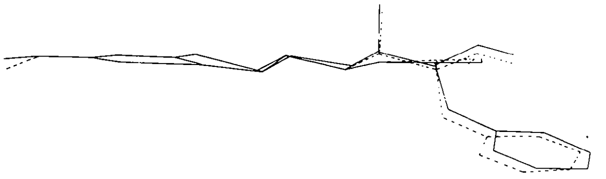


Fig. 2. Superimposed fit of molecule (I) (solid) and molecule (II) (dashed) viewed perpendicular to the C(8)—C(14) bond.

The orientations of the C(17) hydroxy and C(16) hydroxyimino groups exhibit certain differences in molecules (I) and (II). Since molecular-mechanics calculations gave essentially the same geometry for both (I) and (II), it can be concluded that the observed differences in the crystalline state can be attributed to the hydrogen-bond network (Fig. 3).

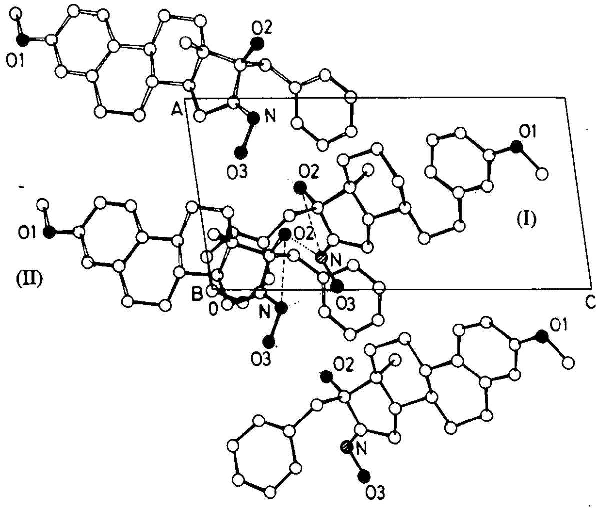


Fig. 3. The hydrogen-bond network viewed along the *b* axis. The intermolecular connections are shown by dotted lines.

Although the positions of the hydroxyl H atoms could not be located in a ΔF map, the observed short interatomic distances suggest that both molecules possess intramolecular hydrogen bonds of the O(2)···N type (Table 2). At the same time, molecules (I) and (II) are linked by intermolecular O(2′)···N and O(3)···N′ hydrogen bonds forming dimer pairs. These dimers are then linked by O(2)···O(3′) intermolecular hydrogen bonds into infinite columns along the *a* axis.

The non-bonded O(1)···O(2) distances [11.053 (7) for molecule (I) and 11.033 (8) Å for molecule (II)], which are responsible for estrogenic activity, are similar to the corresponding distance found in the well known steroid estrogen estradiol (Fullerton, 1977; Duax, Weeks, Rohrer & Griffin, 1977). This is in agreement with observed biological results, *i.e.* biological screening showed that compound (2) exhibits a noticeable residual estrogenic activity, *e.g.* a dose of 25 mg kg^{-1} in experimental animals showed 74.98% agonistic activity (Wakeling, O'Connor & Newboult, 1983).

Experimental

Regioselective addition of benzyllithium to the 17-carbonyl group of 16-hydroxyimino-3-methoxyestra-1,3,5(10)-trien-17-one, (1), afforded a satisfactory yield (68%; m.p. 475–477 K) of the title compound (2). Its structure was deduced on the basis of chemical and spectroscopic evidence. IR (KBR disc): 3550, 3380, 3080, 3020, 1665, 1575, 1050, 1030, 790, 770, 735, 700 cm^{-1}; ^{1}H NMR (DMSO): 0.75 [*s*, 3H, CH_3, C(18)], 3.69 (*s*, 3H, CH_3, CH_3O), 2.8 (*ABq*, 2H, $CH_2C_6H_5$), 4.15 [*s*, 1H, C(17)], 6.60 [*d*, 1H, *J* = 2.6 Hz, H(4)], 7.12 [*dd*, 1H, J_1 = 2.6 Hz, J_2 = 8.4 Hz, H(2)], 7.16 [*d*, 1H, *J* = 8.4 Hz, H(1)], 7.17 [*d*, 2H, *J* = 7.5 Hz, H(2), H(6), phenyl], 7.22 [*t*, 1H, *J* = 7.2 Hz, H(4), phenyl], 7.30 [*t*, 2H, *J* = 7.5 Hz, H(3), H(5), phenyl]; ^{13}C NMR (DMSO): 162.932 [C═NOH, C(16)], 157.558 [$COCH_3$, C(3)], 137.913 (C, aryl), 132.502 (C, aryl), 126.435 (CH, aryl), 125.970 (CH, aryl), 113.950 (CH, aryl), 83.270 [COH, C(17)], 55.342 (OCH_3), 14.953 [C(18)]; mass spectrum: 405 (M^+), 387 ($M^+ - H_2O$); 314, 268, 91; calculated for $C_{26}H_{31}NO_3$: C 77.00, H 7.71, N 3.45%; found: C 76.62, H 7.52, N 4.05%.

Crystal data

$C_{26}H_{31}NO_3$
M_r = 405.54
Triclinic
$P\bar{1}$
a = 7.345 (3) Å
b = 10.532 (3) Å
c = 15.129 (4) Å
α = 102.00 (2)°
β = 100.16 (2)°
γ = 80.99 (3)°
V = 1118.1 (6) Å^3
Z = 2
D_x = 1.20 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 13.3–28.1°
μ = 0.58 mm^{-1}
T = 293 K
Prism
0.300 × 0.075 × 0.025 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–θ scans
Absorption correction: none
2830 measured reflections
2830 independent reflections
2053 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int}$ = 0.0134

$\theta_{\rm max}$ = 55°
$h = 0 \rightarrow 7$
$k = -11 \rightarrow 11$
$l = -16 \rightarrow 15$
3 standard reflections monitored every 3 reflections
frequency: 180 min
intensity decay: none

Refinement

Refinement on F
$R = 0.067$
$wR = 0.068$
$S = 2.42$
2053 reflections
279 parameters
$w = 1/[\sigma^2(F) + 0.023461F^2]$
$(\Delta/\sigma)_{\max} = 0.205$
$\Delta\rho_{\max} = 0.259$ e Å^{-3}
$\Delta\rho_{\min} = -0.159$ e Å^{-3}
Atomic scattering factors from *SHELX*86 (Sheldrick, 1985)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(1)	−0.2158 (10)	−0.7457 (8)	−0.3614 (5)	0.053 (2)
C(2)	−0.1753 (11)	−0.6562 (8)	−0.2839 (5)	0.056 (2)
C(3)	−0.2955 (11)	−0.6266 (8)	−0.2180 (5)	0.054 (2)
C(4)	−0.4493 (10)	−0.6884 (7)	−0.2313 (5)	0.051 (2)
C(5)	−0.4893 (10)	−0.7812 (7)	−0.3112 (5)	0.048 (2)
C(6)	−0.6619 (11)	−0.8493 (9)	−0.3209 (5)	0.063 (2)
C(7)	−0.7292 (10)	−0.9112 (8)	−0.4204 (5)	0.057 (2)
C(8)	−0.5651 (10)	−0.9897 (7)	−0.4607 (5)	0.045 (2)
C(9)	−0.4255 (8)	−0.8998 (7)	−0.4675 (5)	0.046 (2)
C(10)	−0.3755 (10)	−0.8085 (7)	−0.3772 (5)	0.048 (2)
C(11)	−0.2569 (9)	−0.9794 (7)	−0.5108 (6)	0.054 (2)
C(12)	−0.3154 (10)	−1.0648 (6)	−0.6047 (6)	0.054 (2)
C(13)	−0.4607 (8)	−1.1523 (6)	−0.5975 (5)	0.040 (2)
C(14)	−0.6247 (8)	−1.0664 (7)	−0.5597 (5)	0.041 (2)
C(15)	−0.7762 (10)	−1.1543 (7)	−0.5725 (5)	0.049 (2)
C(16)	−0.7346 (9)	−1.2495 (6)	−0.6594 (5)	0.043 (2)
C(17)	−0.5614 (9)	−1.2263 (6)	−0.6883 (5)	0.043 (2)
C(18)	−0.3659 (11)	−1.2581 (7)	−0.5418 (5)	0.054 (2)
C(25)	−0.9384 (12)	−1.1488 (10)	−0.8451 (7)	0.073 (2)
C(19)	−0.6039 (11)	−1.1439 (7)	−0.7656 (5)	0.055 (2)
C(20)	−0.7450 (12)	−1.1893 (7)	−0.8469 (5)	0.056 (2)
C(21)	−0.6930 (14)	−1.2669 (9)	−0.9228 (5)	0.071 (3)
C(22)	−0.8192 (18)	−1.3100 (10)	−1.0013 (7)	0.081 (3)
C(23)	−1.0021 (18)	−1.2770 (11)	−1.0005 (7)	0.085 (3)
C(24)	−1.0690 (14)	−1.1915 (12)	−0.9211 (9)	0.099 (3)
C(26)	−0.3895 (14)	−0.4769 (9)	−0.0848 (6)	0.080 (3)
N	−0.8249 (8)	−1.3425 (5)	−0.7015 (4)	0.046 (2)
O(1)	−0.2502 (9)	−0.5301 (6)	−0.1435 (4)	0.074 (2)
O(2)	−0.4576 (7)	−1.3473 (4)	−0.7273 (3)	0.052 (1)
O(3)	−0.9865 (7)	−1.3489 (5)	−0.6669 (4)	0.063 (1)
C(1′)	−0.5522 (13)	−1.1683 (9)	−0.1787 (6)	0.073 (2)
C(2′)	−0.5333 (15)	−1.2597 (9)	−0.2584 (6)	0.076 (3)
C(3′)	−0.6899 (14)	−1.2765 (8)	−0.3249 (6)	0.069 (3)
C(4′)	−0.8518 (13)	−1.1960 (9)	−0.3129 (6)	0.070 (2)
C(5′)	−0.8713 (11)	−1.1081 (7)	−0.2322 (5)	0.054 (2)
C(6′)	−1.0576 (12)	−1.0188 (9)	−0.2237 (6)	0.069 (2)
C(7′)	−1.0782 (11)	−0.9552 (8)	−0.1265 (6)	0.059 (2)
C(8′)	−0.9058 (10)	−0.8934 (7)	−0.0769 (5)	0.044 (2)
C(9′)	−0.7358 (9)	−1.0045 (7)	−0.0699 (5)	0.045 (2)
C(10′)	−0.7215 (11)	−1.0926 (8)	−0.1627 (5)	0.055 (2)
C(11′)	−0.5588 (10)	−0.9467 (8)	−0.0212 (6)	0.059 (2)
C(12′)	−0.5844 (10)	−0.8705 (8)	0.0759 (5)	0.056 (2)
C(13′)	−0.7490 (9)	−0.7629 (7)	0.0707 (5)	0.047 (2)
C(14′)	−0.9237 (9)	−0.8250 (7)	0.0205 (5)	0.046 (2)
C(15′)	−1.0817 (9)	−0.7138 (8)	0.0368 (5)	0.056 (2)
C(16′)	−1.0166 (10)	−0.6393 (7)	0.1290 (5)	0.049 (2)
C(17′)	−0.8162 (9)	−0.6928 (6)	0.1643 (5)	0.043 (2)
C(18′)	−0.7043 (13)	−0.6541 (8)	0.0269 (6)	0.068 (2)
C(25′)	−1.1172 (13)	−0.7655 (11)	0.2894 (7)	0.084 (3)
C(19′)	−0.8164 (11)	−0.7895 (7)	0.2283 (6)	0.063 (2)
C(20′)	−0.9384 (13)	−0.7412 (8)	0.3010 (5)	0.060 (2)
C(21′)	−0.8699 (16)	−0.6632 (10)	0.3818 (5)	0.086 (3)
C(22′)	−0.985 (3)	−0.6079 (13)	0.4436 (10)	0.121 (5)
C(23′)	−1.162 (3)	−0.6349 (17)	0.4291 (13)	0.130 (6)
C(24′)	−1.2379 (19)	−0.7127 (18)	0.3500 (15)	0.131 (6)
C(26′)	−0.5426 (19)	−1.4665 (10)	−0.4119 (7)	0.098 (4)
N′	−1.0958 (8)	−0.5379 (5)	0.1782 (5)	0.050 (1)
O(1′)	−0.6892 (11)	−1.3619 (7)	−0.4056 (4)	0.098 (2)
O(2′)	−0.7048 (7)	−0.5961 (5)	0.2146 (4)	0.064 (1)
O(3′)	−1.2762 (7)	−0.4997 (5)	0.1319 (4)	0.065 (1)

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

The values given in square brackets are those obtained from molecular-mechanics calculations.

	Molecule (I)	Molecule (II)
C(13)—C(17)	1.555 (8) [1.560]	1.579 (9) [1.560]
C(15)—C(16)	1.525 (9) [1.507]	1.489 (9) [1.499]
C(16)—C(17)	1.486 (10) [1.513]	1.535 (8) [1.522]
C(17)—O(2)	1.447 (6) [1.418]	1.416 (7) [1.416]
C(16)—N	1.265 (7) [1.284]	1.289 (8) [1.286]
N—O(3)	1.395 (8) [1.439]	1.425 (7) [1.437]
C(3)—O(1)	1.383 (9) [1.362]	1.357 (9) [1.371]
C(26)—O(1)	1.443 (11) [1.415]	1.415 (12) [1.410]
C(16)—C(17)—O(2)	111.8 (5) [111.4]	114.5 (6) [110.8]
C(20)—C(17)—O(2)	104.6 (5) [108.1]	106.4 (6) [108.7]
C(15)—C(16)—N	126.8 (6) [124.3]	130.9 (7) [124.7]
C(17)—C(16)—N	121.8 (6) [121.9]	118.1 (6) [121.7]
C(16)—N—O(3)	114.6 (6) [122.4]	109.6 (6) [122.0]
C(2)—C(3)—O(1)	116.2 (7) [120.0]	124.6 (9) [124.5]
C(4)—C(3)—O(1)	124.0 (7) [124.3]	116.2 (8) [119.3]
C(3)—O(1)—C(26)	117.7 (7) [123.6]	117.5 (8) [123.3]
C(12)—C(13)—C(17)—O(2)	82.3 (7) [88.4]	79.9 (8) [89.3]
C(20)—C(19)—C(17)—O(2)	71.0 (7) [67.0]	76.1 (8) [68.4]
C(15)—C(16)—C(17)—O(2)	144.0 (6) [134.9]	143.0 (6) [135.1]
O(2)—C(17)—C(16)—N	−32.5 (9) [−44.0]	−33.4 (9) [−44.8]
C(17)—C(16)—N—O(3)	−178.6 (6) [179.9]	177.1 (6) [179.9]
C(2)—C(3)—O(1)—C(26)	166.8 (7) [177.5]	20.3 (14) [0.4]
C(4)—C(3)—O(1)—C(26)	−10.8 (12) [−2.6]	−165.0 (9) [−179.0]

Bridgehead distances for potential hydrogen bonds

O(2)···N	2.785 (7)	O(3)···N′$^{\rm i}$	2.828 (8)
O(2′)···N′	2.821 (8)	O(2)···O(3′$^{\rm ii}$)	2.793 (7)
N···O(2′$^{\rm i}$)	2.788 (7)		

Symmetry codes: (i) $x, y-1, z-1$; (ii) $1+x, y-1, z-1$.

Table 3. *Ring-puckering coordinates and asymmetry parameters*

Ring	Molecule	Q (Å)	φ (°)	θ (°)	C_s (°)	C_2 (°)
B	(I)	0.516 (9)	151 (1)	46 (1)		2.0 [C(7)—C(8)]
	(II)	0.500 (10)	155 (2)	42 (1)		2.8 [C(7)—C(8)]
C	(I)	0.605 (8)	130 (7)	174.0 (8)	5.7 [C(8)]	8.5 [C(8)—C(9)]
					6.6 [C(9)]	5.3 [C(9)—C(11)]
					1.0 [C(11)]	3.9 [C(11)—C(12)]
	(II)	0.610 (9)	163 (9)	177.7 (8)	2.1 [C(8)]	3.1 [C(8)—C(9)]
					3.3 [C(9)]	2.9 [C(9)—C(11)]
					1.3 [C(11)]	2.5 [C(11)—C(12)]
D	(I)	0.437 (8)	188 (1)		8.4 [C(13)]	12.3 [C(16)]
	(II)	0.462 (9)	187 (1)		8.7 [C(13)]	12.3 [C(16)]

H atoms were generated and refined as riding groups (overall isotropic displacement parameters were refined for different CH types). The positions of the hydroxyl H atoms could not be located in the ΔF map.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *CSU*88 (Vicković, 1988).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: KA1137). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 2040–2042

4,4′-Oxybispyridine and 4,4′-Selenobispyridine

Simon J. Dunne,[a] Ellak I. von Nagy-Felsobuki[a] and Maureen F. Mackay[b]

[a]*Department of Chemistry, The University of Newcastle, Callaghan, NSW, Australia 2308, and* [b]*School of Chemistry, La Trobe University, Bundoora, Victoria, Australia 3083. E-mail: xraymm2@lure.latrobe.edu.au*

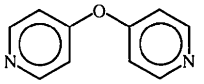
(*Received 21 July 1995; accepted 27 October 1995*)

Abstract

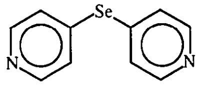
4,4′-Oxybispyridine, $C_{10}H_8N_2O$, and 4,4′-selenobispyridine, $C_{10}H_8N_2Se$, both adopt twist conformations, with twist angles of 69.2 (2) and 65.7 (2)°, respectively. In the oxy compound, the C—O bond lengths are 1.375 (4) and 1.373 (4) Å, with the C—O—C angle 121.1 (2)°. In the seleno compound, the C—Se bond lengths are 1.913 (3) and 1.913 (4) Å, with the angle at the Se atom 100.40 (14)°. The asymmetric coordination to the chalcogen atom, evidenced by the dissimilar exocyclic angles at the bridgehead C atoms, is no doubt a consequence of steric interaction between the proximal H atoms *ortho* to the latter.

Comment

The stereochemistry of the diphenyl and dipyridyl chalcogenides has been investigated by a variety of physical and theoretical techniques, leading to conflicting conclusions as to their preferred conformations (Higgasi & Uyeo, 1939; Higgasi & Smyth, 1960; Rolla & Sanesi, 1962; Fong, 1964; Cumper, Read & Vogel, 1965; Anderson & Smyth, 1965; Montaudo, Finocchiaro, Trivellone, Bottino & Maravigna, 1971; Pappalardo & Pistara, 1972; Montaudo, Bottino & Trivellone, 1972; Montaudo, Finocchiaro & Caccamese, 1973; Krivdin & Kalabin, 1982). Our earlier theoretical and photoelectron studies on the chalcogenobispyridines (Dunne, Summers & von Nagy-Felsobuki, 1991, 1992*a*,*b*, 1993) provided evidence for a limited range of conformers in the gas phase, but the paucity of structural data on these systems hampered a quantitative analysis of the energetics of conformer interconversion. Thus, in order to further complement the structural database on this class of compounds, we now report the crystal structures of 4,4′-oxybispyridine, (1), and 4,4′-selenobispyridine, (2).



(1)



(2)

4,4′-Oxybispyridine adopts a twist conformation as defined by the torsion angles C4′—O1—C4—C3 and C4—O1—C4′—C5′† of 30.8 (2) and 49.2 (2)°, respectively. The dihedral angle between the pyridine rings of 69.9 (3)°, the C—O—C angle of 121.1 (3)° and the C—O bond lengths of 1.375 (4) and 1.373 (4) Å lie close to the values found for these dimensions in 2,2′-oxybispyridine [69.9 (5), 120.3(3)°, 1.378 (6) and 1.395 (6) Å, respectively; Dunne, von Nagy-Felsobuki & Mackay, 1995].

4,4′-Selenobispyridine also adopts a twist conformation as defined by the torsion angles C4′—Se1—C4—C3 and C4—Se1—C4′—C5′ of 19.2 (2) and 59.0 (2)°, respectively, with the dihedral angle between the pyridine ring planes being 65.7 (2)° [*cf.* 52.5 (3)° in 2,2′-selenobispyridine; Dunne, von Nagy-Felsobuki & Mackay, 1995]. The Se—C bond lengths are 1.913 (3) and 1.913 (4) Å, and the C—Se—C angle is 100.4 (1)°, compared with values of 1.920 (4), 1.940 (4) Å and 101.9 (2)°, respectively, found in 2,2′-selenobispyridine.

As observed in other bridged diphenyls (van der Heijden *et al.*, 1975), the two exocyclic angles at the bridgehead atoms, C4 and C4′, are dissimilar. In compound (1), those enclosed by the adjacent pyridyl moiety are significantly larger at 121.9 (3) and 123.6 (3)° (O1—C4′—C5′ and O1—C4—C3, respectively), compared with 117.3 (4) and 117.6 (3)° (O1—C4—C5 and O1—C4′—C3′), and in compound (2) these values are 123.0 (2) and 122.4 (3)° (Se1—C4—C3 and Se1—C4′—C5′, respectively) compared with 119.7 (3) and 119.1 (3)° (Se1—C4′—C3′ and Se1—C4—C5). The resultant twisting of the two rings away from each other most probably arises from steric interaction between the H3 and H5′ atoms in both structures. It is of interest to note that the 2,2′-oxybispyridine molecule adopts a

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† Refer to convention of van der Heijden, Griffith, Chandler & Robertson (1975) for bridged diphenyls.