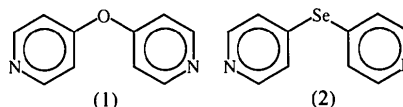


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Anderson & Smyth, 1965; Montaudo, Finocchiaro, Trivellone, Bottino & Maravigna, 1971; Pappalardo & Pistara, 1972; Montaudo, Bottino & Trivellone, 1972; Montaudo, Finocchiaro & Caccamese, 1973; Krivdin & Kalabin, 1982). Our earlier theoretical and photoelectron 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).



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4,4'-Oxybispyridine and 4,4'-Selenobispyridine

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Abstract

4,4'-Oxybispyridine, C₁₀H₈N₂O, and 4,4'-selenobispyridine, C₁₀H₈N₂Se, 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;

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

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

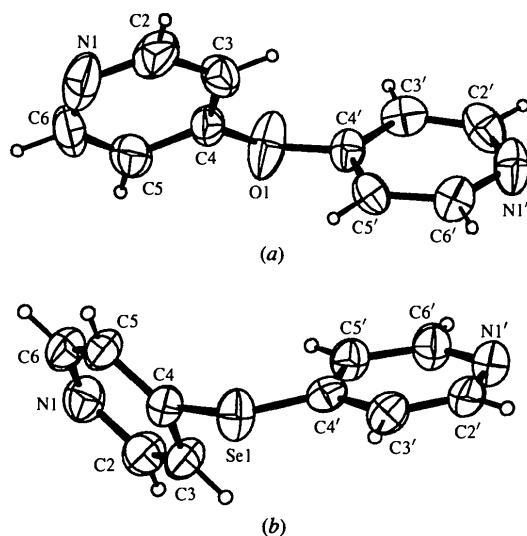


Fig. 1. Perspective views of the molecular structures of (a) 4,4'-oxybispyridine and (b) 4,4'-selenobispyridine, with displacement ellipsoids scaled to 30% and 50% probabilities, respectively. H atoms are denoted by spheres of arbitrary radii.

skew conformation, whereas the 2,2'-selenobispyridine molecule adopts a twist conformation, as is also observed for the two title compounds. The ring N atoms, being *ortho* to the bridgehead C atoms in the 2,2'- analogues, apparently preclude a twist conformation in the 2,2'-oxy analogue. In the 2,2'-seleno analogue, however, in which the pyridine rings are further apart [the spacing between the bridgehead C atoms being 2.997 (5) and 2.405 Å in the respective molecules], a twist conformation is allowed. The endocyclic C—N—C angles, which have a mean value of 116.8 (2)° in compound (1) and 116.6 (4)° in (2), and the C—N bond lengths, which have a mean value of 1.311 (5) Å in (1) and 1.333 (4) Å in (2), are similar to values reported for other pyridine structures.

Experimental

Compound (1) was prepared by the method of Rockley & Summers (1981) and (2) was prepared by the method of Boduzek & Wiczorek (1983). Both compounds were recrystallized from hexane.

Compound (1)

Crystal data

$C_{10}H_8N_2O$
 $M_r = 172.2$
 Orthorhombic
 $P2_12_12_1$
 $a = 8.809 (1) \text{ \AA}$
 $b = 10.420 (1) \text{ \AA}$
 $c = 9.642 (1) \text{ \AA}$
 $V = 885.0 (2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.292 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation
 $\lambda = 1.5418 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 20\text{--}28^\circ$
 $\mu = 0.70 \text{ mm}^{-1}$
 $T = 291 (2) \text{ K}$
 Irregular prism
 $0.31 \times 0.26 \times 0.21 \text{ mm}$
 Colourless

Data collection

Rigaku AFC diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 gaussian (SHELX76;
 Sheldrick, 1976)
 $T_{\min} = 0.845$, $T_{\max} = 0.876$
 1636 measured reflections
 741 independent reflections
 535 observed reflections
 $[I > 2\sigma(I)]$

Refinement

Refinement on F^2
 $R(F) = 0.048$
 $wR(F^2) = 0.098$
 $S = 0.838$
 741 reflections
 119 parameters
 H atoms: see text
 $w = 1/[\sigma^2(F_o^2) + (0.0402P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.100 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.121 \text{ e \AA}^{-3}$

$R_{\text{int}} = 0.026$
 $\theta_{\max} = 65.0^\circ$
 $h = -10 \rightarrow 10$
 $k = 0 \rightarrow 12$
 $l = 0 \rightarrow 11$
 3 standard reflections
 monitored every 100 reflections
 intensity decay: <2.0%

Extinction correction:
 SHELXL93 (Sheldrick, 1993)

Extinction coefficient:
 0.056 (3)

Atomic scattering factors
 from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (1)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O1	0.0934 (4)	0.1848 (3)	1.0911 (3)	0.118 (1)
N1	0.2166 (6)	-0.1927 (3)	1.0390 (5)	0.118 (2)
C2	0.2834 (5)	-0.1036 (4)	0.9664 (5)	0.108 (2)
C3	0.2441 (4)	0.0242 (3)	0.9778 (4)	0.082 (1)
C4	0.1336 (4)	0.0595 (3)	1.0668 (3)	0.071 (1)
C5	0.0594 (5)	-0.0328 (5)	1.1405 (4)	0.099 (1)
C6	0.1071 (7)	-0.1587 (5)	1.1229 (5)	0.113 (2)
N1'	0.1176 (4)	0.4748 (3)	0.8027 (4)	0.099 (1)
C2'	0.1657 (4)	0.4864 (4)	0.9294 (5)	0.090 (1)
C3'	0.1660 (4)	0.3925 (4)	1.0259 (4)	0.075 (1)
C4'	0.1066 (4)	0.2764 (3)	0.9892 (4)	0.063 (1)
C5'	0.0513 (4)	0.2577 (3)	0.8594 (4)	0.068 (1)
C6'	0.0614 (4)	0.3601 (4)	0.7698 (4)	0.080 (1)

Table 2. Geometric parameters (\AA , °) for (1)

O1—C4	1.373 (4)	O1—C4'	1.375 (4)
N1—C2	1.304 (5)	N1'—C2'	1.299 (5)
N1—C6	1.308 (6)	N1'—C6'	1.332 (5)
C2—C3	1.380 (5)	C2'—C3'	1.350 (5)
C3—C4	1.349 (4)	C3'—C4'	1.365 (4)
C4—C5	1.363 (5)	C4'—C5'	1.357 (4)
C5—C6	1.388 (6)	C5'—C6'	1.376 (5)
C4—O1—C4'	121.1 (2)	C2'—N1'—C6'	115.4 (3)
C2—N1—C6	118.2 (5)	N1'—C2'—C3'	125.6 (4)
N1—C2—C3	122.0 (4)	C2'—C3'—C4'	117.6 (3)
C2—C3—C4	119.7 (4)	O1—C4'—C5'	117.6 (3)
O1—C4—C3	123.6 (3)	O1—C4'—C5'	121.9 (3)
O1—C4—C5	117.3 (4)	C3'—C4'—C5'	120.3 (3)
C3—C4—C5	119.0 (4)	C4'—C5'—C6'	116.4 (3)
C4—C5—C6	117.3 (4)	N1'—C6'—C5'	124.8 (3)
N1—C6—C5	123.7 (5)		

Compound (2)

Crystal data

$C_{10}H_8N_2Se$
 $M_r = 235.1$

Cu $K\alpha$ radiation
 $\lambda = 1.5418 \text{ \AA}$

Triclinic

$P\bar{1}$
 $a = 8.609 (2) \text{ \AA}$
 $b = 5.769 (2) \text{ \AA}$
 $c = 10.478 (3) \text{ \AA}$
 $\alpha = 72.81 (4)^\circ$
 $\beta = 70.12 (2)^\circ$
 $\gamma = 80.92 (3)^\circ$
 $V = 466.6 (2) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.674 \text{ Mg m}^{-3}$

Cell parameters from 25

reflections
 $\theta = 19\text{--}35^\circ$
 $\mu = 5.16 \text{ mm}^{-1}$
 $T = 291 (1) \text{ K}$
 Platelet
 $0.25 \times 0.18 \times 0.02 \text{ mm}$
 Pale yellow

C4—Se1—C4'	100.40 (14)	C2'—N1'—C6'	117.2 (3)
C2—N1—C6	115.9 (3)	N1'—C2'—C3'	124.0 (3)
N1—C2—C3	125.2 (4)	C2'—C3'—C4'	118.5 (4)
C2—C3—C4	117.7 (3)	C5'—C4'—C3'	117.9 (3)
C5—C4—C3	117.8 (3)	C5'—C4'—Se1	122.4 (3)
C5—C4—Se1	119.1 (3)	C3'—C4'—Se1	119.7 (3)
C3—C4—Se1	123.0 (2)	C4'—C5'—C6'	119.9 (3)
C6—C5—C4	119.1 (3)	N1'—C6'—C5'	122.4 (4)
N1—C6—C5	124.4 (3)		

H atoms were included at calculated positions and allowed to ride on the corresponding C atoms. Calculations were performed on a VAX 8800 computer.

For both compounds, data collection: *Rigaku AFC Software* (Rigaku Corporation, 1974); cell refinement: *Rigaku AFC Software*; data reduction: *Rigaku AFC Software*; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL93*.

Data collection

Rigaku AFC diffractometer
 $w/2\theta$ scans
 Absorption correction:
 gaussian (*SHELX76*;
 Sheldrick, 1976)
 $T_{\min} = 0.291$, $T_{\max} = 0.822$
 1558 measured reflections
 1472 independent reflections
 1309 observed reflections
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 65.0^\circ$
 $h = -9 \rightarrow 10$
 $k = -6 \rightarrow 6$
 $l = 0 \rightarrow 12$
 3 standard reflections
 monitored every 100
 reflections
 intensity decay: $<2.7\%$

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1056). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Refinement

Refinement on F^2
 $R(F) = 0.039$
 $wR(F^2) = 0.105$
 $S = 1.068$
 1472 reflections
 119 parameters
 H atoms: see text
 $w = 1/[\sigma^2(F_o^2) + (0.0656P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.511 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.537 \text{ e \AA}^{-3}$

Extinction correction:
SHELXL93 (Sheldrick,
 1993)
 Extinction coefficient:
 0.0041 (11)
 Atomic scattering factors
 from *International Tables*
 for *Crystallography* (1992),
 Vol. C, Tables 4.2.6.8 and
 6.1.1.4)

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 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (2)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Se1	0.69635 (6)	-0.06716 (7)	0.56832 (4)	0.0482 (2)
N1	0.9037 (5)	0.5788 (6)	0.1744 (3)	0.0508 (8)
C2	0.9113 (5)	0.5719 (7)	0.2998 (4)	0.0471 (9)
C3	0.8521 (5)	0.3918 (6)	0.4211 (4)	0.0416 (8)
C4	0.7758 (4)	0.2044 (6)	0.4124 (3)	0.0338 (7)
C5	0.7653 (5)	0.2106 (7)	0.2819 (4)	0.0426 (8)
C6	0.8307 (5)	0.3969 (8)	0.1690 (4)	0.0482 (9)
N1'	0.6576 (4)	0.2323 (6)	0.9507 (3)	0.0490 (8)
C2'	0.7509 (5)	0.0336 (7)	0.9274 (4)	0.0503 (10)
C3'	0.7680 (5)	-0.0593 (6)	0.8153 (4)	0.0415 (8)
C4'	0.6821 (4)	0.0616 (6)	0.7208 (3)	0.0351 (7)
C5'	0.5847 (5)	0.2680 (7)	0.7442 (4)	0.0420 (8)
C6'	0.5751 (5)	0.3492 (8)	0.8584 (4)	0.0493 (9)

Table 4. Geometric parameters (\AA , $^\circ$) for (2)

Se1—C4	1.913 (3)	C5—C6	1.364 (5)
Se1—C4'	1.913 (4)	N1'—C2'	1.327 (5)
N1—C2	1.326 (5)	N1'—C6'	1.350 (5)
N1—C6	1.330 (5)	C2'—C3'	1.385 (6)
C2—C3	1.379 (5)	C3'—C4'	1.393 (5)
C3—C4	1.390 (5)	C4'—C5'	1.378 (5)
C4—C5	1.389 (5)	C5'—C6'	1.383 (6)