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2,2′-Oxybispyridine and 2,2′-Selenobispyridine

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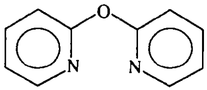
Abstract

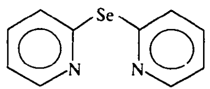
The oxy structure ($C_{10}H_8N_2O$) adopts a skew conformation with the skew angle 69.9 (4)°; the angle at the O atom is 120.3 (3)° and the O—C distances are 1.378 (6) and 1.395 (6) Å. The seleno structure ($C_{10}H_8N_2Se$) adopts a twist conformation with the twist angle 52.5 (3)°; the angle at the Se atom is 101.9 (2)° and the Se—C distances are 1.920 (4) and 1.940 (4) Å.

Comment

Studies investigating the gas-phase and solution structures of the diphenyl and dipyridyl chalcogenides have led to a variety of conclusions regarding the stereochemistry of these systems (Higgasi & Uyeo, 1939; Rolla & Sanesi, 1962; Fong, 1964; Cumper, Read & Vogel, 1965; Anderson & Smyth, 1965; Pappalardo & Pistara, 1972; Montaudo, Finocchiaro & Caccamese, 1973). More recently, NMR data have indicated substantially non-planar equilibrium structures for diphenyl ethers with interplanar angles in the range 20–50° (Krivdin & Kalabin, 1982). Photoelectron studies by Dunne, Summers & von Nagy-Felsobuki (1991, 1992*a*,*b*, 1993) on the chalcogenobispyridines have now provided evidence for the existence of a range of conformers in the gas phase, but were best modelled at the *ab initio* level using the skew conformer. The scarcity of structural data on the parent compounds has made the accuracy of these earlier studies difficult to determine. To complement our earlier theoretical and photoelectron spectroscopic studies on the chalcogenobispyridines, we now report the crystal structures of the title compounds.



(1)



(2)

2,2′-Oxybispyridine, (1), adopts a skew conformation as defined by the torsional angles C2′—O1—C2—N1 and C2—O1—C2′—C3′ of 0.0 (6) and −73.3 (6)°, respectively, with the lone pair on N1 in the proximal position and that on N1′ in the distal position.* The dihedral angle between the pyridine rings of 69.9 (4)°, the C—O—C angle of 120.3 (3)° and the C—O bond lengths of 1.378 (6) and 1.395 (6) Å lie close to comparable values reported for bis(phenyl) ethers; *cf.* 73.2 (3), 119.6 (3)°, 1.374 (3) and 1.383 (3) Å in bis(3,4-dichlorophenyl) ether (Singh & McKinney, 1980), 64.5 (3), 119.9 (2)°, 1.379 (2) and 1.398 (2) Å in 2,2′-bis(tosylmethylphenyl) ether (Stepien, Wajsman, Grabowski, Glinka & Lecocq, 1987), and 68.4 (8), 120.6 (6)°, 1.376 (8) Å in bis(2,4-dichlorophenyl) ether (Rissanen, Valkonen & Virkki, 1988).

2,2′-Selenobispyridine, (2), on the other hand, adopts a twist conformation defined by the torsional angles C2—Se1—C2′—N1′ of 42.2 (3)° and C2′—Se1—C2—C3 of 25.3 (3)°. The lone pair on N1 occupies the distal position whilst on N1′ it is proximal.* The dihedral angle between the pyridine ring planes is 52.5 (3)° and the C—Se1—C angle is 101.9 (2)°, compared with the analogous values of 55 and 106 (2)° in di-*p*-tolylselenide (Blackmore & Abrahams, 1955). The more acute C—Se1—C angle of 101.9 (2)° in (2) and 106 (2)° in the tolylselenide compared with the C—O—C angle in (1) may restrict the adoption of a skew conformation, as observed in the latter despite the longer Se1—C bonds of 1.920 (4) and 1.940 (4) Å in (2) and 1.92 (5) and 1.93 (5) Å in the tolylselenide. These distances are also similar to those of 1.93 (5) Å found in diphenyl-

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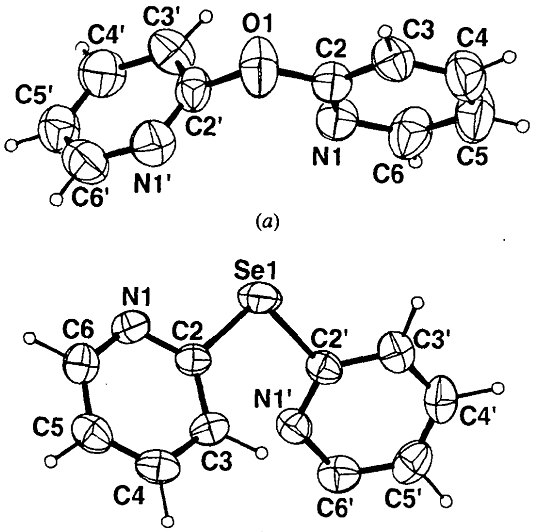
* Refer to the convention of van der Heijden, Griffith, Chandler & Robertson (1975).



(a)

(b)

Fig. 1. Perspective views of the molecular structures of (a) (1), and (b) (2), with displacement ellipsoids scaled to 50% probability. H atoms are shown as spheres of arbitrary radius.

diselenide (Marsh, 1952), 1.93 (3) and 1.95 (3) Å in di-*p*-tolylselenium dichloride and di-*p*-tolylselenium dibromide, respectively (McCullough & Marsh, 1950), and 1.929 (6) Å in 3-selenocyanatopyridine (Dunne, Summers, von Nagy-Felsobuki & Mackay, 1994).

As observed in other bridged diphenyl complexes (van der Heijden, Griffith, Chandler & Robertson, 1975), the two exocyclic angles at each of the bridgehead atoms, C2 and C2′, are dissimilar in (1); those enclosed by the adjacent pyridyl moiety are larger at 118.0 (3) and 121.4 (4)° compared with the other two at 115.5 (3) and 113.3 (4)°, whereas in (2) the comparable values are 124.5 (2), 118.4 (3) and 111.6 (2) and 116.7 (2)°. The resulting twisting of the two rings from each other no doubt arises from steric interactions between N1 and H3′ in (1) and between N1′ and H3 in (2). The endocyclic C—N—C angles, which have a mean value of 114.7 (5)° in (1) and 116.8 (2)° in (2), and the C—N bond lengths which have a mean value of 1.326 (8) Å in (1) and 1.332 (5) Å in (2), are similar to values reported for other pyridine structures.

Experimental

(1) was prepared by the method of Villiers & den Hertog (1957) and (2) by adaption of the method reported by Dunne, Summers & von Nagy-Felsobuki (1992*c*). Crystals for both compounds were obtained from light petroleum (b.p. 333–353 K).

Compound (1)

Crystal data

$C_{10}H_8N_2O$
$M_r = 172.2$
Monoclinic
$P2_1/n$
$a = 8.651\,(2)$ Å
$b = 11.534\,(3)$ Å
$c = 8.878\,(3)$ Å
$\beta = 93.60\,(2)°$
$V = 884.1\,(8)$ Å^3
$Z = 4$
$D_x = 1.294$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 18–30°$
$\mu = 0.66$ mm^{-1}
$T = 291\,(1)$ K
Platelet
0.31 × 0.26 × 0.09 mm
Colourless

Data collection

Rigaku AFC diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (Sheldrick, 1976)
$T_{\min} = 0.822$, $T_{\max} = 0.946$
1550 measured reflections
1454 independent reflections
697 observed reflections $[I > 3.0\sigma(I)]$

$R_{\rm int} = 0.031$
$\theta_{\max} = 65.0°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 10$
3 standard reflections monitored every 50 reflections intensity variation: <2.5%

Refinement

Refinement on F
$R = 0.057$
$wR = 0.075$
$S = 1.52$
697 reflections
151 parameters
All H-atom coordinates refined
$w = 1/[\sigma^2(F) + 0.00165F^2]$
$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}

Extinction correction: *SHELX*76 (Sheldrick, 1976)
Extinction coefficient: $F_c = F(1 - xF^2/\sin\theta)$, $x = 7.6\,(3) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

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

$$B_{\rm eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
O1	1.0055 (4)	0.4508 (3)	0.1976 (5)	6.1 (1)
N1	0.7943 (5)	0.3795 (3)	0.3139 (5)	4.3 (1)
C2	0.8507 (5)	0.4575 (4)	0.2247 (5)	3.9 (1)
C3	0.7697 (6)	0.5457 (5)	0.1509 (6)	4.4 (1)
C4	0.6156 (6)	0.5523 (6)	0.1726 (6)	5.8 (2)
C5	0.5490 (6)	0.4727 (6)	0.2649 (8)	6.5 (2)
C6	0.6421 (6)	0.3908 (5)	0.3332 (8)	5.6 (2)
N1′	1.1475 (5)	0.2892 (4)	0.1662 (5)	5.0 (1)
C2′	1.0979 (5)	0.3632 (4)	0.2640 (6)	4.1 (1)
C3′	1.1431 (6)	0.3651 (5)	0.4141 (6)	5.2 (2)
C4′	1.2449 (6)	0.2816 (5)	0.4683 (8)	5.5 (2)
C5′	1.2975 (6)	0.2023 (5)	0.3722 (6)	4.9 (2)
C6′	1.2478 (8)	0.2101 (5)	0.2239 (8)	5.4 (2)

Table 2. *Geometric parameters* (Å, °) *for* (1)

O1—C2	1.378 (6)	C5—C6	1.359 (9)
O1—C2′	1.395 (6)	N1′—C2′	1.309 (7)
N1—C2	1.313 (6)	N1′—C6′	1.339 (8)
N1—C6	1.345 (8)	C2′—C3′	1.365 (8)
C2—C3	1.377 (6)	C3′—C4′	1.371 (8)
C3—C4	1.361 (8)	C4′—C5′	1.350 (9)
C4—C5	1.380 (9)	C5′—C6′	1.362 (9)
C2—O1—C2′	120.3 (3)	C2′—N1′—C6′	115.0 (4)
C2—N1—C6	114.4 (5)	O1—C2′—N1′	113.3 (4)

O1—C2—N1	118.0 (3)	O1—C2′—C3′	121.4 (4)
O1—C2—C3	115.5 (3)	N1′—C2′—C3′	124.9 (4)
N1—C2—C3	126.6 (4)	C2′—C3′—C4′	118.0 (5)
C2—C3—C4	116.6 (4)	C3′—C4′—C5′	119.3 (5)
C3—C4—C5	119.7 (5)	C4′—C5′—C6′	117.9 (5)
C4—C5—C6	118.0 (5)	N1′—C6′—C5′	124.9 (5)
N1—C6—C5	124.6 (5)		

Compound (2)

Crystal data

$C_{10}H_8N_2Se$
$M_r = 235.2$
Monoclinic
$P2_1/a$
$a = 12.370\ (1)$ Å
$b = 5.977\ (1)$ Å
$c = 13.909\ (1)$ Å
$\beta = 113.10\ (1)^\circ$
$V = 945.9\ (4)$ Å^3
$Z = 4$
$D_x = 1.651$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 20$–38°
$\mu = 5.09$ mm^{-1}
$T = 291\ (1)$ K
Prismatic
0.38 × 0.31 × 0.26 mm
Pale yellow

Data collection

Rigaku AFC diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (Sheldrick, 1976)
$T_{\min} = 0.241$, $T_{\max} = 0.404$
1656 measured reflections
1585 independent reflections
1313 observed reflections $[I > 3.5\sigma(I)]$

$R_{\rm int} = 0.018$
$\theta_{\max} = 65.0^\circ$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 16$
3 standard reflections monitored every 50 reflections intensity variation: <3.4%

Refinement

Refinement on F
$R = 0.041$
$wR = 0.056$
$S = 3.71$
1313 reflections
119 parameters
H-atom treatment: see text
$w = 1/[\sigma^2(F) + 0.00015F^2]$
$(\Delta/\sigma)_{\max} = 0.005$
$\Delta\rho_{\max} = 0.56$ e Å^{-3}
$\Delta\rho_{\min} = -0.58$ e Å^{-3}

Extinction correction: *SHELX*76 (Sheldrick, 1976)
Extinction coefficient: $F_c = F(1 - xF^2/\sin\theta)$, $x = 2.27\ (7) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

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

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Se1	0.24979 (4)	0.16197 (7)	0.25696 (3)	4.64 (2)
N1	0.4009 (3)	0.0696 (5)	0.1652 (2)	3.66 (7)
C2	0.3154 (3)	−0.0305 (5)	0.1832 (2)	3.09 (7)
C3	0.2751 (3)	−0.2441 (6)	0.1488 (3)	3.55 (8)
C4	0.32811 (4)	−0.3604 (6)	0.0947 (3)	4.09 (9)
C5	0.4172 (4)	−0.2600 (7)	0.0740 (3)	4.40 (10)
C6	0.4508 (3)	−0.0450 (7)	0.1113 (3)	4.27 (10)
N1′	0.2435 (2)	−0.2339 (5)	0.3626 (2)	3.60 (7)
C2′	0.1805 (3)	−0.0520 (6)	0.3210 (2)	3.28 (8)
C3′	0.0746 (3)	−0.0013 (7)	0.3251 (3)	4.04 (8)
C4′	0.0296 (3)	−0.1471 (8)	0.3760 (3)	4.62 (10)
C5′	0.0916 (4)	−0.3413 (7)	0.4192 (3)	4.65 (11)
C6′	0.1967 (4)	−0.3791 (7)	0.4095 (3)	4.20 (9)

Table 4. *Geometric parameters* (Å, °) *for* (2)

Se1—C2	1.940 (4)	C5—C6	1.387 (6)
Se1—C2′	1.940 (4)	N1′—C2′	1.331 (4)
N1—C2	1.322 (5)	N1′—C6′	1.345 (6)
N1—C6	1.332 (6)	C2′—C3′	1.367 (6)
C2—C3	1.386 (5)	C3′—C4′	1.371 (7)
C3—C4	1.366 (7)	C4′—C5′	1.391 (6)
C4—C5	1.381 (7)	C5′—C6′	1.377 (7)
C2—Se1—C2′	101.9 (2)	C2′—N1′—C6′	116.6 (2)
C2—N1—C6	117.1 (2)	Se1—C2′—N1′	116.7 (2)
Se1—C2—N1	111.6 (2)	Se1—C2′—C3′	118.4 (3)
Se1—C2—C3	124.5 (2)	N1′—C2′—C3′	124.8 (3)
N1—C2—C3	123.9 (2)	C2′—C3′—C4′	118.1 (3)
C2—C3—C4	118.3 (3)	C3′—C4′—C5′	119.1 (3)
C3—C4—C5	119.2 (3)	C4′—C5′—C6′	118.4 (3)
C4—C5—C6	118.1 (3)	N1′—C6′—C5′	123.0 (3)
N1—C6—C5	123.3 (3)		

The structure of the seleno compound was solved by the heavy atom method and that of the oxy compound by direct methods. The structures were refined by full-matrix least squares using *SHELX*76 (Sheldrick, 1976). The H-atom coordinates for (2) were calculated and the atoms given the same isotropic displacement factor as the atom to which they are bonded. 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: *SHELX*76 (Sheldrick, 1976); program(s) used to refine structures: *SHELX*76; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *Xtal*3.0 (Hall & Stewart, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1016). 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. (1995). **C51**, 1457–1459

o-Phénylènediammonium Dihydrogéno-diphosphate

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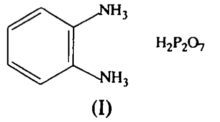
Abstract

The main feature of $(NH_3C_6H_4NH_3)H_2P_2O_7$ is the existence of $H_2P_2O_7$ groups connected in pairs by strong hydrogen bonds. The pairs are further linked by hydrogen bonds to form infinite ribbons spreading parallel to the *a* axis.

Commentaire

La synthèse de l'*o*-phénylènediammonium dihydrogénodiphosphate (I) entre dans le cadre d'une étude systématique de l'intéraction des diamines aromatiques avec l'acide diphosphorique. Nous décrivons dans ce travail la préparation et l'étude cristalline du diphosphate $(NH_3C_6H_4NH_3)H_2P_2O_7$ (Fig. 1). L'aspect essentiel à dégager de cet arrangement atomique (Fig. 2) est l'existence de groupements $(H_2P_2O_7)^{2-}$ fortement liés entre eux par la liaison hydrogène (O31···O12 2,497 Å) en paires. Chacune d'elles est liée à deux voisines par quatre liaisons hydrogène O32···O11 (2,647 Å), en un ruban infini parallèle à la direction *a*. Ce type de ruban diffère des enchaînements d'unités diphosphates $(H_2P_2O_7)_n$ décrits précédemment dans



(I)

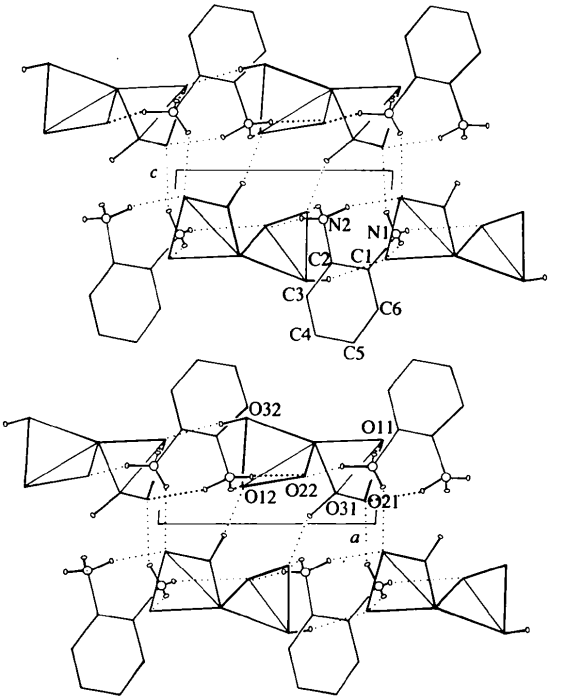


Fig. 1. Projection selon l'axe *b* de la structure de l'*o*-phénylènediammonium dihydrogénodiphosphate.

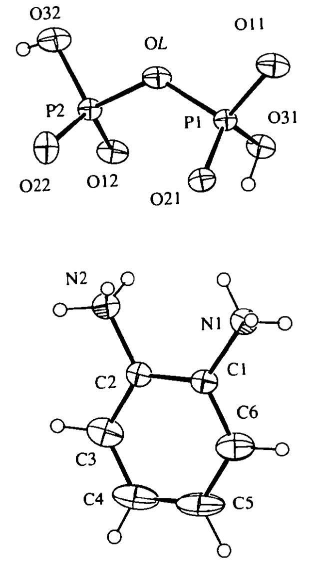


Fig. 2. Vue en perspective de l'unité asymétrique de $(NH_3C_6H_4NH_3)$-$H_2P_2O_7$. Les ellipsoïdes correspondent à 50% de probabilité et les atomes d'hydrogène sont représentés par des cercles de diamètres arbitraires.

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