For all compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1977); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structures: *MULTAN* (Main *et al.*, 1980); program(s) used to refine structures: *MolEN*; molecular graphics: *ORTEP* (Johnson, 1976); software used to prepare material for publication: *MolEN*.

DJB thanks the National Science Foundation for support of this work

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1152). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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α,α′-Bis(2-pyridylseleno)-*p*-xylene

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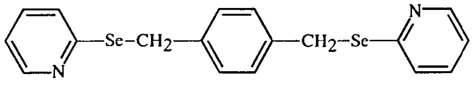
Abstract

The title compound, $C_{18}H_{16}N_2Se_2$, crystallizes with two half molecules per asymmetric unit. Each independent molecule displays crystallographic inversion symmetry. The pyridyl rings are oriented such that the N atoms are *endo* to the methylene groups. The —Se—CH_2— bridges display extended conformations.

Comment

The title compound, (I), crystallizes with two half molecules per asymmetric unit. The second halves are generated by inversion symmetry at the centres of the rings C31–C36 at (1/2,0,0) and C41–C46 at (0,0,0) (Fig. 1). Where appropriate, values for the second molecule are given in square brackets in the discussion below.



(I)

The relative orientation of the Se- and N-atom pairs across the central phenyl ring is *trans* as a result of the inversion symmetry. The orientation of the N atoms can be regarded as *endo* (or *cis*) relative to the neighbouring methylene groups, as indicated by the torsion angle C1—Se1—C11—N1 = 9.2 (3)° [C2—Se2—C21—N2 = −4.2 (3)°]. The bridges between rings display extended conformations, C31—C1—Se1—C11 = 164.7 (3)° [C41—C2—Se2—C21 = −164.6 (3)°].

The interplanar angle between the phenyl (C31–C36) and the adjacent pyridine (C11–N1) rings is 66.7 (2)° [63.3 (3)° (phenyl C41–C46 and pyridine C21–N2)].

The C—C—Se angles at the methylene C atoms are tetrahedral at 109.2 (2)°. The angles at the Se atoms, 98.6 (3)° [99.3 (2)°], are in agreement with reported values for comparable compounds (with a methylene group and an aromatic ring attached to the Se atom) ranging from 100.5 (3) to 101.6 (2)° (Brussani, Ley, Wright & Williams, 1986; Dupont, Dideberg & Jacquemin, 1990; Iwaoka & Tomoda, 1994). The same is true for the Se—CH_2 and the Se—C(aryl) bond lengths with values of 1.957 (3) Å [1.959 (4) Å] and 1.909 (4) Å [1.909 (4) Å], respectively, compared with the corresponding values for the above-cited compounds ranging from 1.940 (3) to 1.966 (8) Å (Se—CH_2) and from 1.913 (4) to 1.924 (8) Å (Brussani *et al.*, 1986; Dupont *et al.*, 1990; Iwaoka & Tomoda, 1994).

The molecules pack in 'herringbone' layers in the planes 202 (Fig. 2). The interplanar angles between the two independent phenyl and pyridine rings are 23.1 (6) and 4.0 (2)°, respectively.

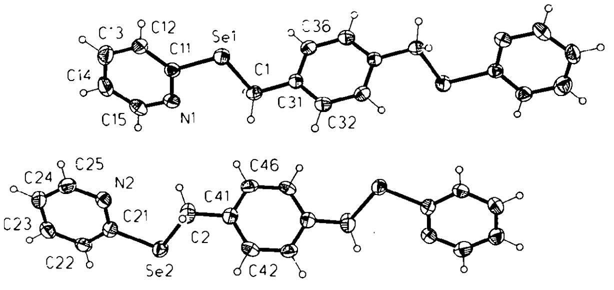


Fig. 1. The two independent molecules of the title compound in the crystal. Ellipsoids correspond to the 50% probability level. H-atom radii are arbitrary. Only the asymmetric unit is numbered.

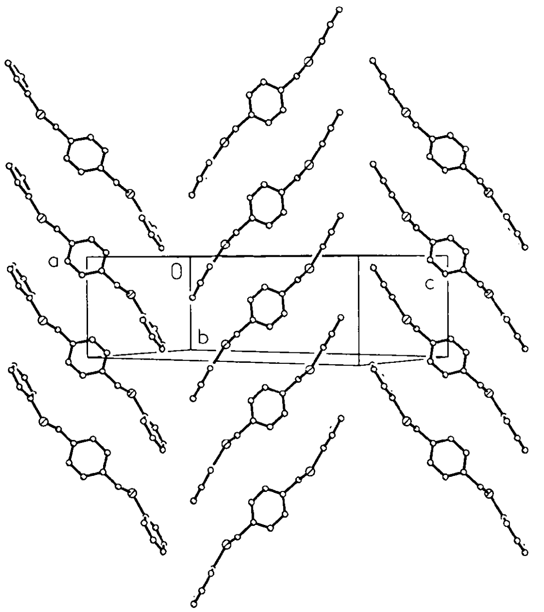


Fig. 2. Packing diagram of the title compound (H atoms omitted).

Experimental

The title compound was prepared in 60% yield from the reaction between sodium 2-pyridineselenolate and α,α'-dibromo-p-xylene. The required solution of the selenolate in THF was prepared by treatment of the corresponding selenol (Mautner, Chu & Lee, 1962; Kienitz, Thöne & Jones, 1996) with excess sodium hydride followed by filtration of the resulting colourless solution. The pure product was obtained by removal of the solvent, extraction with diethyl ether and chromatography over a silica column with a mixture of ethyl acetate:light petroleum (1:2) (second fraction). Single crystals were obtained from toluene/petroleum ether 30/40 at 243 K.

Crystal data

$C_{18}H_{16}N_2Se_2$
$M_r = 418.25$
Monoclinic
$P2_1/c$
$a = 11.628\,(3)$ Å
$b = 6.804\,(2)$ Å
$c = 20.778\,(5)$ Å
$\beta = 96.12\,(3)°$
$V = 1634.6\,(8)$ Å^3
$Z = 4$
$D_x = 1.700$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 58 reflections
$\theta = 10$–$11.5°$
$\mu = 4.521$ mm^{-1}
$T = 143\,(2)$ K
Irregular needle
$0.80 \times 0.15 \times 0.10$ mm
Colourless

Data collection

Stoe Stadi-4 diffractometer
ω/θ-scans
Absorption correction: ψ scans (*XEMP*; Siemens, 1994*a*)
$T_{\min} = 0.46$, $T_{\max} = 0.64$
3123 measured reflections
2869 independent reflections
2270 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0240$
$\theta_{\max} = 25.03°$
$h = -13 \rightarrow 1$
$k = 0 \rightarrow 8$
$l = -24 \rightarrow 24$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F)[F^2 > 2\sigma(F^2)] = 0.0313$
$wR(F^2) = 0.0850$
$S = 1.067$
2856 reflections
199 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2 + 1.3872P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.385$ e Å^{-3}
$\Delta\rho_{\min} = -0.532$ e Å^{-3}
Extinction correction: none
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 (Å^2)*

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

	x	y	z	$U_{\rm eq}$
Se1	0.44547 (3)	0.37947 (6)	0.14005 (2)	0.03292 (13)
Se2	−0.20698 (3)	0.37583 (6)	0.08560 (2)	0.03553 (13)
N1	0.2412 (3)	0.6001 (4)	0.12092 (14)	0.0314 (7)
N2	−0.0942 (3)	0.6250 (5)	0.17965 (14)	0.0322 (7)
C1	0.3557 (3)	0.2678 (6)	0.0637 (2)	0.0303 (8)
C2	−0.0480 (3)	0.2775 (7)	0.0999 (2)	0.0430 (10)
C11	0.3457 (3)	0.5934 (5)	0.1552 (2)	0.0274 (8)
C12	0.3857 (3)	0.7340 (6)	0.1998 (2)	0.0348 (9)
C13	0.3153 (4)	0.8922 (6)	0.2093 (2)	0.0450 (10)
C14	0.2079 (4)	0.9043 (6)	0.1741 (2)	0.0417 (10)
C15	0.1752 (3)	0.7575 (6)	0.1310 (2)	0.0388 (10)
C21	−0.1937 (3)	0.5958 (5)	0.1430 (2)	0.0296 (8)
C22	−0.2886 (3)	0.7213 (6)	0.1426 (2)	0.0353 (9)
C23	−0.2788 (4)	0.8832 (6)	0.1818 (2)	0.0428 (10)
C24	−0.1758 (4)	0.9173 (6)	0.2204 (2)	0.0428 (10)
C25	−0.0877 (4)	0.7862 (6)	0.2174 (2)	0.0389 (10)
C31	0.4304 (3)	0.1292 (5)	0.0310 (2)	0.0255 (7)
C32	0.4105 (3)	−0.0694 (5)	0.0313 (2)	0.0339 (9)
C36	0.5212 (3)	0.1981 (6)	−0.0011 (2)	0.0338 (9)
C41	−0.0252 (3)	0.1364 (5)	0.0474 (2)	0.0298 (8)
C42	−0.0834 (3)	−0.0413 (6)	0.0399 (2)	0.0323 (9)
C46	0.0585 (3)	0.1754 (5)	0.0068 (2)	0.0331 (9)

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

Se1—C11	1.909 (4)	N1—C15	1.347 (5)
Se1—C1	1.957 (3)	N2—C21	1.331 (5)
Se2—C21	1.909 (4)	N2—C25	1.345 (5)
Se2—C2	1.959 (4)	C1—C31	1.494 (5)
N1—C11	1.342 (5)	C2—C41	1.497 (5)
C11—Se1—C1	98.6 (2)	N1—C11—Se1	118.1 (3)
C21—Se2—C2	99.3 (2)	C12—C11—Se1	118.2 (3)
C11—N1—C15	116.3 (3)	N1—C15—C14	124.0 (4)
C21—N2—C25	116.5 (3)	N2—C21—C22	123.4 (3)
C31—C1—Se1	109.2 (2)	N2—C21—Se2	118.8 (3)
C41—C2—Se2	110.3 (2)	C22—C21—Se2	117.7 (3)
N1—C11—C12	123.7 (3)	N2—C25—C24	124.3 (4)

Data collection: *DIF*4 (Stoe & Cie, 1994*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1994*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP*5 (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*93.

We thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1204). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Stoe & Cie (1994*b*). *REDU4. Data Reduction Program.* Version 7.08. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1996). C**52**, 2849–2851

(8*R*,8a*S*)-Indolizidine-1-spiro-2′-(1′,3′-dithiane)-8-carbonitrile

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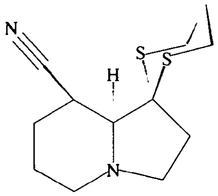
Abstract

The title compound, $C_{12}H_{18}N_2S_2$, is an indolizidine whose structure was determined unequivocably by X-ray diffraction. The indolizidine ring adopts a *trans*-fused envelope–chair conformation while the dithiane ring adopts a chair conformation distal to the nitrile moiety.

Comment

Numerous routes to the indolizidine ring system have been reported (for a recent example, see Carretero & Arrayas, 1995, and references therein), largely stimulated by their extremely potent inhibition of glycosidases (Elbein, 1987). Our synthesis of the indolizidine ring system stems from our ability to perform conjugate additions to unsaturated nitriles (Fleming & Pak, 1995) that serves to assemble rapidly heterocyclic indolizidines, quinolizidines (Hussain, Fleming, Norman & Chang, 1996) and azulenes.

The X-ray structure of the title compound, (I), shows that the indolizidine ring system adopts the envelope–chair orientation found in both the crystalline state (Koh, Lee, Sim & Zhu, 1993) and in solution (Reymond, Pinkerton & Vogel, 1991). The metric parameters of the rings are quite similar to the indolizidine 1-deoxycastanospermine (Koh, Lee, Sim & Zhu, 1993) and, in the present case, differ mainly in the shortening of the N(1)—C(9) bond [1.459 (4) *versus* 1.479 (5) Å] and lengthening of C(7)—C(8) [1.550 (4) *versus* 1.522 (5) Å] and C(8)—C(9) [1.528 (4) *versus* 1.514 (5) Å]. A similar though less-pronounced trend is seen in the homologous quinolizine (Hussain, Fleming, Norman & Chang, 1996).



(I)

The exact reason for these trends are unclear though we may explain this phenomenon by an interaction between the electron-rich N atom and the strongly electron-withdrawing nitrile group (Reddy, Goldstein &

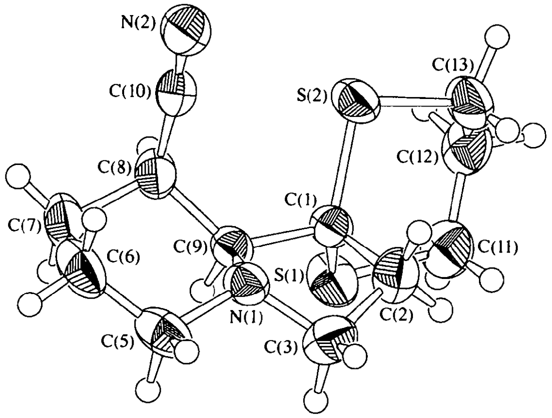


Fig. 1. Perspective drawing of (8*R*,8a*S*)-indolizidine-1-spiro-2′-(1′,3′-dithiane)-8-carbonitrile with displacement ellipsoids drawn at the 50% probability level.

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