# Diquino[4,3-b;3′,4′-e][1,4]thiaselenine

Céline Besnard,[a] Christian Kloc,[b] Theo Siegrist,[b] Christer Svensson[c] and Krystian Pluta[d]*

[a]Laboratoire de Cristallographie, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland, [b]Bell Laboratories, Lucent Technologies, Mountain Avenue, Murray Hill, NJ 07974, USA, [c]Department of Materials Chemistry, Lund University, Lund, Sweden, and [d]Department of Organic Chemistry, Medical University of Silesia, Jagiellońska 4, 41-200 Sosnowiec, Poland

Correspondence e-mail:
pluta@slam.katowice.pl

The title compound, $C_{18}H_{10}N_2SSe$, is a pentacyclic ring system folded along the S···Se vector. The central thiaselenine ring adopts a boat conformation and the two halves of the molecule are related by a crystallographic mirror plane.

Comment

Pentacyclic heterocycles are considered as a new type of electron donor (Boros & Harfenist, 1998; Ahmad et al., 1996; Marti et al., 1994; Engman et al., 1988). They show photoelectric properties (Yoshida et al., 1994) and constitute the active layer in a field-effect transistor (FET) device (Miao et al., 2003). Diareno-1,4-thiaselenines and diheteroareno-1,4-thiaselenines have very seldom been the subject of X-ray crystallographic analysis (Meyers et al., 1988; Dotze et al., 1991; Nowak et al., 2002). The purpose of this study is to confirm the structure of the title compound, (I), previously assessed on the basis of spectroscopic properties (^{1}H NMR and MS; Pluta, 1994), and to compare it with the structure of the isomeric pentacycle (III) (Nowak et al., 2002).

(I)   (II)   (III)
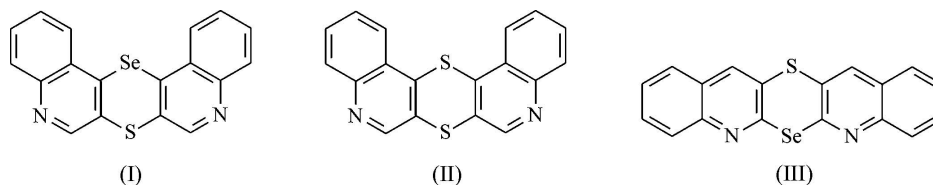
The angular condensed diquinothiaselenine, (I), is isostructural with its sulfur analogue, diquinodithiine, (II) (Besnard et al., 2006). A crystallographic mirror plane passes through the S and Se atoms (Fig. 1). As observed for (III), the pentacyclic ring system in (I) is folded along the S···Se vector, with very slight folding along the C3—C4 and C3′—C4′ bonds. This results in a butterfly shape. The angle between the planes of the two quinoline ring systems is 131.5 (2)°, and the dihedral angle between the planes defined by the atoms of the two halves of the central ring (i.e. S/Se/C3/C4 and S/Se/C3′/C4′) is 125.5 (2)°. These angles show that pentaphene (I) is more folded than the isomeric pentacene (III) [153.20 (7) and 138.97 (7)°, respectively; Nowak et al., 2002].

The thiaselenine ring of (I) adopts a boat conformation, with atoms S and Se in the bow and stern positions, displaced from the basal plane (C/3/C4/C/3′/C4′) by 0.707 (5) and 0.729 (4) Å, respectively. Whereas the C—S and C—Se bond lengths in (I) are similar to those found in (III), the C—S—C and C—Se—C bond angles are definitely smaller, by about 4.4 and 6.2°, respectively.
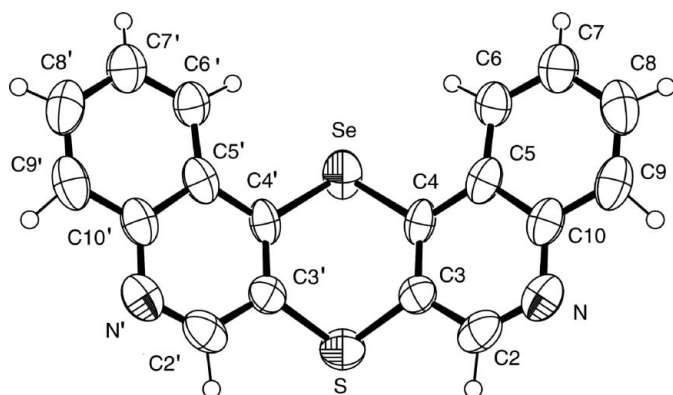
Figure 1
A view of the title compound, showing the atom-labelling scheme and with displacement ellipsoids drawn at the 50% probability level. Primed atoms are generated by the symmetry operator $(1 - x, y, z)$.
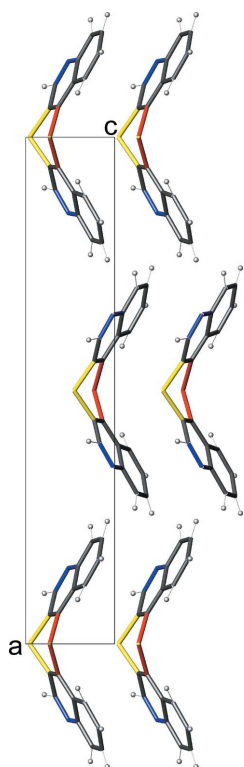

Figure 2
The crystal packing of (I), viewed along the *b* axis.

There are very close contacts between atoms H61/H61′ and Se (2.704 Å), which are shorter than the sum of the van der Waals radii (H + Se = 3.1 Å; Bondi, 1964). These steric interactions cause deshielding of the H61/H61′ atoms in the ¹H NMR spectrum (Pluta, 1994). Similar close contacts are found between atoms H21/H21′ and S (2.674 Å).

In the crystal structure, the molecules are stacked in columns along the short *c* axis. This allows π–π interactions to occur between adjacent molecules, the mean distance between the quinoline planes being 3.62 (2) Å (Fig. 2).

In conclusion, the present X-ray crystallographic analysis has fully confirmed the proposed structure of (I) and that, during the ring opening–ring closure transformations from (II)

to (I), the Smiles rearrangement was not observed as it was during the synthesis of (II) (Pluta, 1991).

Experimental

The title pentacycle, (I), was obtained in a few steps from pentacycle (II), *via* dithiine ring opening and thiaselenine ring closure, according to the reported procedure of Pluta (1991). Similarly to (II), solvent-grown crystals of (I) were of insufficient quality, and only the horizontal vapour-transport method (Laudise *et al.*, 1998) produced crystals suitable for X-ray analysis. Single crystals were grown by horizontal vapour transport in a flow of argon gas at 1 atm (1 atm = 101325 Pa). The evaporation zone was kept at 525 K, while the growth zone remained at room temperature. Crystals nucleated spontaneously on the wall of the furnace tube and grew in the temperature gradient between the evaporation and room-temperature zones. Details of the experimental apparatus have been reported elsewhere (Laudise *et al.*, 1998).

Crystal data

$C_{18}H_{10}N_2SSe$	$D_x = 1.696$ Mg m^{-3}
$M_r = 365.32$	Synchrotron radiation
Orthorhombic, $Pmn2_1$	$\lambda = 1.089$ Å
$a = 23.625$ (3) Å	$\mu = 2.77$ mm^{-1}
$b = 7.3299$ (9) Å	$T = 293$ K
$c = 4.1297$ (5) Å	Needle, yellow
$V = 715.13$ (15) Å^3	$0.03 \times 0.001 \times 0.001$ mm
$Z = 2$	

Data collection

Mar CCD area-detector diffractometer	770 independent reflections
φ scans	684 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{int} = 0.030$
3727 measured reflections	$\theta_{max} = 32.7°$

Refinement

Refinement on F^2	where T_i are the Chebychev
$R[F^2 > 2\sigma(F^2)] = 0.024$	polynomials and $x = F_c/F_{max}$
$wR(F^2) = 0.052$	(Prince, 1982; Watkin, 1994)
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
770 reflections	$\Delta\rho_{max} = 0.14$ e Å^{-3}
104 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
H-atom parameters constrained	Absolute structure: Flack (1983),
$w = [1 - (F_o - F_c)^2/36\sigma^2(F)]^2/$	with 72 Friedel pairs
$\quad [23.9T_o(x) - 32.3T_1(x)$	Flack parameter: 0.420 (19)
$\quad + 11.2T_2(x)]$	

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.303 (6)	C3—S	1.779 (5)
N1—C10	1.363 (7)	C4—Se	1.912 (4)
C3—C4	1.350 (6)		
C3—S—C3^i	99.9 (4)	C4—Se—C4^i	96.0 (3)

Symmetry code: (i) $-x + 1, y, z$.

The H atoms were located in a difference Fourier map and refined as riding in their as-found positions, with C—H = 0.87–0.99 Å and $U_{iso}(H) = 1.4U_{eq}$(carrier atom). Refinement of the Flack (1983) parameter indicates inversion twinning.

Data collection: *TWINSOLVE* (Rigaku/MSC & Prekat, 2002); cell refinement: *TWINSOLVE*; data reduction: *TWINSOLVE*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993);

program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP-3* (Burnett & Johnson, 1996) and *ATOMS* (Dowty, 1994); software used to prepare material for publication: *CRYSTALS* and *enCIFer* (Allen *et al.*, 2004).

References

Ahmad, A. R., Mehta, L. K. & Parrick, J. (1996). *J. Chem. Soc. Perkin Trans. 1*, pp. 2443–2449.

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Besnard, C., Kloc, C., Siegrist, T., Svensson, C. & Pluta, K. (2006). *Acta Cryst.* E**62**, o1333–o1335.

Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Boros, E. E. & Harfenist, M. (1998). *J. Org. Chem.* **63**, 10045–10047.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Dotze, M., Hinrichs, W. & Klar, G. (1991). *J. Chem. Res.* **314**, M2861–2862.

Dowty, E. (1994). *ATOMS for Windows*. Version 3.0. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Engman, L., Hellberg, J., Ishaq, C. & Söderholm, S. (1988). *J. Chem. Soc. Perkin Trans. 1*, pp. 2095–2101.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Laudise, R. A., Kloc, C., Simpkins, P. G. & Siegrist, T. (1998). *J. Cryst. Growth*, **187**, 449–454.

Marti, C., Irurre, J., Alvarez-Larena, A., Piniella, J. F., Brillas, E., Fajari, L., Alemán, C. & Juliá, L. (1994). *J. Org. Chem.* **59**, 6200–6207.

Meyers, E. A., Irgolic, K. J., Zingaro, R. A., Junk, T., Chakravorty, R., Dereu, N. L. M., French, K. & Pappalardo, G. C. (1988). *Phosphorus Sulfur Silicon*, **938**, 257–269.

Miao, Q., Nquyen, T.-Q., Someya, T., Blanchet, G. B. & Nuckolls, C. (2003). *J. Am. Chem. Soc.* **125**, 10284–10287.

Nowak, M., Pluta, K. & Suwińska, K. (2002). *New J. Chem.* **26**, 1216–1220.

Pluta, K. (1991). *Sulfur Lett.* **13**, 9–18.

Pluta, K. (1994). *Phosphorus Sulfur Silicon*, **92**, 149–154.

Prince (1982). *Mathematical Techniques in Crystallography and Material Science*. New York: Springer-Verlag.

Rigaku/MSC and Prekat (2002). *TWINSOLVE*. Rigaku/MSC, The Woodlands, Texas, USA, and Prekat AB, Lund, Sweden.

Watkin (1994). *Acta Cryst.* A**50**, 411–437.

Yoshida, S., Nozawa, K., Sato, N. & Uchida, T. (1994). *Bull. Chem. Soc. Jpn*, **67**, 2017–2023.