# Diquino[3,4-b;4',3'-e][1,4]dithiine

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, Sweden, and [d]Department of Organic Chemistry, The Medical University of Silesia, Jagielloñska 4, 41-200 Sosnowiec, Poland

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

Key indicators

In the title compound, $C_{18}H_{10}N_2S_2$, a crystallographic mirror plane passes through the two S atoms. The pentacyclic ring system is folded along the S—S vector and the central dithiine ring adopts a boat conformation.

Comment

Thia- and azapentacycles are considered to be a new type of electron donor (Boros et al., 1998; Ahmad et al., 1996; Marti et al., 1994; Engman et al., 1988), which show photoelectric properties (Yoshida et al., 1994) and constitute the active layer in a field-effect transistor (FET) device (Miao et al., 2003). The diazadithiapentaphenes (I) and (II) (common names: isothioquinanthrene and thioquinanthrene, respectively) and the diazadithiapentacenes (III) and (IV) have proved to be excellent substrates in the search for new quinoline derivatives via 1,4-dithiine ring-opening reactions (e.g. Nowak et al., 2002; Bębenek et al., 2003; Pluta, 2005).
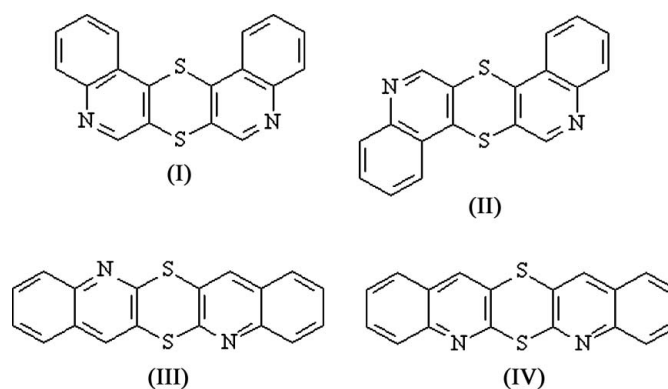
Although the pentacycles (I)–(IV) have been known for many years, there have been some doubts regarding their correct structures, which differ only in the structural symmetry, C_{2h} and C_{2v} (Dreikorn et al., 1979; Maślankiewicz & Pluta, 1980; Nowak et al., 2003), the more so because they can be interconverted through the Smiles rearrangement [(II) → (I), (III) → (IV); Pluta, 1991; Nowak et al., 2003). The structure of (I) was determined on the basis of spectroscopic properties and chemical transformations (Maślankiewicz & Pluta, 1980; Pluta, 1994; Maślankiewicz et al., 1998). Since spectroscopic data are indirect and chemical transformations can proceed with isomerization and rearrangement, only X-ray crystallographic analysis can unequivocally determine the actual structure.

The structure of (II) was confirmed by X-ray crystallographic examination of its dihydrochloride [crystals of neat (II) obtained from common solvents were not suitable]
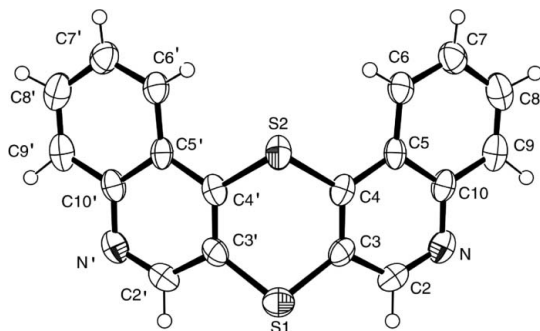
Figure 1
View of the title compound, showing the atom-labelling scheme and displacement ellipsoids drawn at the 50% probability level. [Symmetry code for primed atoms: $-x$, y, z.]
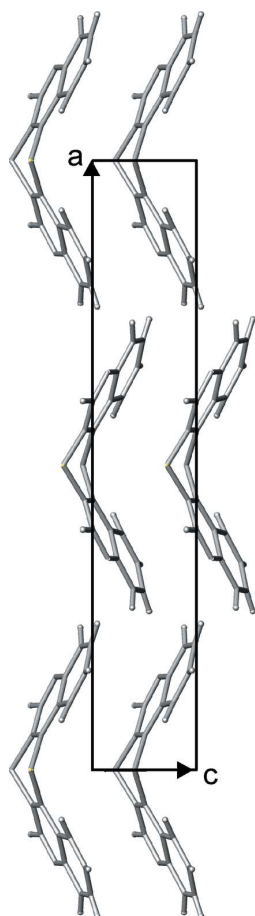

Figure 2
The crystal packing, viewed along the b axis.

(Maślankiewicz et al., 1990). Similarly, solvent-grown crystals of (I) were of insufficient quality, and only the horizontal vapor-transport method (Laudise et al., 1998) produced crystals suitable for X-ray analysis. The purpose of this study was to determine the structure of (I) and compare it with the structures of the isomeric pentacycles (II)–(IV) Maślankiewicz et al., 1990, Nowak et al., 2003).

A crystallographic mirror plane passes through atoms S1 and S2 (Fig. 1). As for (II)–(IV), the pentacyclic ring system in (I) is folded along the S—S 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 134.55 (9)°, and the dihedral angle beetwen the planes defined by the atoms of the two halves of the central ring (i.e. S1/S2/C3/C4 and S1/S2/C3'/C4') is 129.73 (16)°. These angles show that pentaphenes (I) and (II) are more folded than the isomeric pentacenes (III) and (IV). The dithiine ring adopts a boat conformation, with atoms S1 and S2 in the bow and stern positions, displaced from the basal plane (C/3/C4/C/3'/C4') by 0.617 (5) and 0.659 (5) Å, respectively. The average length of the C—S bond in (I) (1.768 (3) Å) is very similar to that found in (II)–(IV) but the C—S—C bond angles are smaller than in (III) and (IV) (Table 1).

There are very close contacts between atoms H61/H61' and S2 (2.599 Å), which are shorter than the sum of the van der Waals radii (H + S = 3.0 Å; Bondi, 1964). These steric interactions cause deshielding of the H61/H61' protons in the ^{1}H NMR spectra (Pluta, 1994). Similar close contacts are found between atoms H21/H21' and S1 (2.727 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 3.55 (1) Å (Fig. 2).

In conclusion, the X-ray crystallographic analysis has fully confirmed the proposed structure of (I), supporting earlier evidence for the unprecedented type of Smiles rearrangement during the 1,4-dithiine ring-opening reaction of (II) to form (I).

Experimental

Pentaphene (I) was obtained from the reaction of pentaphene (II) with sodium methanethiolate in dimethyl sulfoxide, according to a reported procedure (Pluta, 1991). Single crystals were grown by horizontal vapor transport in a flow of argon gas at 1 atm. The evaporation zone was kept at 523 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 by Laudise et al. (1998).

Crystal data

$C_{18}H_{10}N_2S_2$	Synchrotron radiation
$M_r = 318.42$	$\lambda = 0.9020$ Å
Orthorhombic, $Pmn2_1$	Cell parameters from 2883
$a = 23.440$ (5) Å	reflections
$b = 7.5873$ (15) Å	$\theta = 3.4$–$34.4°$
$c = 3.9960$ (8) Å	$\mu = 0.37$ mm^{-1}
$V = 710.7$ (3) Å^3	$T = 293$ K
$Z = 2$	Needle, colourless
$D_x = 1.488$ Mg m^{-3}	$0.2 \times 0.01 \times 0.01$ mm

Data collection

Siemens SMART CCD	1157 independent reflections
diffractometer	1157 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.062$
Absorption correction: multi-scan	$\theta_{max} = 34.4°$
(SADABS; Siemens, 1996)	$h = -24 \rightarrow 28$
$T_{min} = 0.85$, $T_{max} = 0.97$	$k = -9 \rightarrow 9$
2883 measured reflections	$l = -4 \rightarrow 4$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.077$

$S = 0.96$

1157 reflections

104 parameters

H-atom parameters constrained

$w = [1 - (F_o - F_c)^2/36\sigma^2(F)]^2/$
$\quad [15.6T_0(x) + 20.5T_1(x) +$
$\quad 8.37T_2(x)]$
$\quad$ where T_i are Chebychev
$\quad$ polynomials and $x = F_c/F_{max}$
$\quad$ (Prince, 1982; Watkin, 1994)

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.19$ e Å^{-3}

$\Delta\rho_{min} = -0.18$ e Å^{-3}

Absolute structure: Flack (1983), 497 Friedel pairs

Flack parameter: −0.11 (14)

Table 1
Selected geometric parameters (Å, °).

N—C2	1.300 (4)	C3—S1	1.766 (3)
N—C10	1.373 (4)	C4—S2	1.772 (3)
C3—C4	1.371 (4)		
C4^i—S2—C4	100.34 (16)	C3—S1—C3^i	100.52 (18)

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

The H atoms were located in a difference Fourier map and refined as riding in their as-found positions; C—H = 0.87–0.98 Å and U_{iso}(H) = 1.5U_{eq}(carrier atom). Although the Friedel pairs were not merged and a Flack (1983) parameter was refined, the small anomalous differences at the experimental wavelength and the small number of measured Friedel pairs mean that this parameter is unreliable. However, since the molecule is achiral, this does not influence the discussion of the molecular geometry.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEPIII* (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.

Bębenek, E., Chrobak, E. & Maślankiewicz, A. (2003). *Heterocycles*, **60**, 2065–2075.

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

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

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

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

Dowty, E. (1994) *ATOMS for Windows*. Version 3.0. Shape Software, Kingsport, TN, USA.

Dreikorn, B. A., Elsasser, F. E. & Jourdan, G. P. (1979). *J. Org. Chem.* **44**, 877–880.

Engman, L., Hellberg, J., Ishaq, C. & Söderholm, S. (1988). *J. Chem. Soc. Perkin Trans. I*, 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.

Maślankiewicz, A. & Pluta, K. (1980). *Pol. J. Chem.* **54**, 33–40.

Maślankiewicz, A., Pluta, K., Wyszomirski, M., Gogoll, A. & Maślankiewicz, M. J. (1998). *Magnetic Res. Chem.* **36**, 73–75.

Maślankiewicz, A., Wyszomirski, M. & Głowiak T. (1990). *J. Crystallogr. Spectrosc. Res.* **20**, 375–380.

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

Morak, B., Pluta, K., Suwińska, K., Grymel, M., Besnard, C., Schiltz, M., Kloc, C. & Siegrist, T. (2005). *Heterocycles* **65**, 2619–2634.

Nowak, M., Pluta, K., Kloc, C. & Siegrist, T. (2003). *Heterocycles*, **60**, 2045–2056.

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.

Pluta, K. (2005). *Phosphorus Sulfur Silicon*, **180**, 2457–2475.

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

Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wsconsin, USA.

Siemens (1996). *SADABS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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

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