organic papers

2,3-Bis(5-bromothien-2-yl)quinoxaline

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2,3-Bis(5-bromothien-2-yl)quinoxaline, $C_{16}H_8Br_2N_2S_2$, is a bromo-substituted 2,3-di(thien-2-yl)quinoxaline which can be easily synthesized by the Schiff base reaction between 1,2-phenylenediamine and 1,2-bis(5-bromothien-2-yl)-1,2-ethanedione. The molecule has twofold non-crystallographic symmetry.

Comment

Following our earlier structural studies on thenoins (Crundwell *et al.*, 2002*a*,*b*) and thenils (Crundwell, Sullivan *et al.*, 2003), and other thiophene-containing molecules such as 2,5-diphenyl-3,4-dithien-3-ylcyclopentadien-1-one (Linehan *et al.*, 2003), 4-bromo-2-thiophenecarboxaldehyde (Stacy *et al.*, 2003), and 2,3-di(thien-2′-yl)quinoxaline (Crundwell, Sayers *et al.*, 2003), we report the structure of 2,3-bis(5-bromothien-2-yl)quinoxaline, (I). Based on complexes involving 2,3-diphenylquinoxaline (Datta *et al.*, 2002), we believe 2,3-di- and 2,3-bis-substituted thienylquinoxalines will make interesting bidentate ligands when combined with soft metal cations such as Cu^I. This quinoxaline crystallizes with one molecule in the asymmetric unit that packs by stacking in an offset head-to-tail manner. The molecule has twofold non-crystallographic symmetry and the quinoxaline moiety displays a slight deviation from planarity due to steric interactions between 5-bromothien-2-yl rings. The angle between the mean plane of the quinoxaline and the mean plane of ring 1 (containing S1) is 23.68 (10)°, whereas the angle between the mean plane of the quinoxaline and the mean plane of ring 2 is 47.41 (7)°. A view of (I) is shown in Fig. 1.

(I)
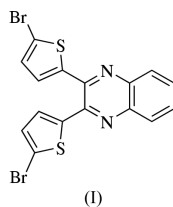
Experimental

The title compound, (I), was obtained by reacting equal amounts of 1,2-phenylenediamine and 1,2-bis(5-bromothien-2-yl)-1,2-ethanedione in boiling 95% ethanol (41% yield). After recrystallization from a 50/50 mixture of 95% ethanol and toluene, crystals of (I) were obtained by slow evaporation. Yellow needles were harvested and had a sharp melting point of 368 K. The ^{1}H NMR (CDCl$_3$, 400 MHz, δ) spectrum consisted of two multiplets at 8.022 (2H, $J = 9.7$ Hz) and 7.726 p.p.m. (2H, $J = 9.7$ Hz) for the quinoxaline H atoms, as well as two doublets for the thienyl ring protons, one doublet from protons at the 3′-positions of the thienyl rings at 7.894 p.p.m. (2H, $J_{3,4} = 4.1$ Hz) and the other doublet from protons at the 4′-positions of the thienyl

rings at 7.183 p.p.m. (2H, $J_{4,3}$ = 4.1 Hz). When compared to the ^{1}H NMR spectrum of 2,3-dithien-2-ylquinoxaline (Lukes *et al.*, 2001), the chemical shift for the proton at the 3′-position of the thienyl ring is shifted significantly downfield. This is most likely due to the lack of free rotation in 5-bromothien-2-yl rings in (I), thereby orienting the 3′-position H atoms in a deshielding zone above the other aromatic thienyl ring.

Crystal data

$C_{16}H_8Br_2N_2S_2$	$Z = 2$
$M_r = 452.18$	$D_x = 1.922$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.8701$ (9) Å	Cell parameters from 7531
$b = 9.0664$ (9) Å	reflections
$c = 11.1751$ (11) Å	$\theta = 1.9$–28.4°
$\alpha = 86.380$ (2)°	$\mu = 5.45$ mm^{-1}
$\beta = 79.998$ (2)°	$T = 100$ (2) K
$\gamma = 62.033$ (2)°	Thick plate, yellow
$V = 781.51$ (13) Å^3	$0.88 \times 0.35 \times 0.14$ mm

Data collection

Bruker SMART APEX diffractometer	3818 independent reflections
	3126 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.044$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	$\theta_{max} = 28.4°$
	$h = -11 \rightarrow 11$
$T_{min} = 0.018$, $T_{max} = 0.466$	$k = -12 \rightarrow 12$
7531 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + (0.0927P)^2]$
$wR(F^2) = 0.119$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.85$	$(\Delta/\sigma)_{max} = 0.001$
3818 reflections	$\Delta\rho_{max} = 1.39$ e Å^{-3}
199 parameters	$\Delta\rho_{min} = -1.08$ e Å^{-3}

H atoms were placed in calculated positions, with a C—H distance of 0.95 Å, and were included in the refinement in riding-model approximation, with $U_{iso} = 1.2U_{eq}$ of the carrier atom.

Data collection: *SMART* (Bruker, 1997–1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997–1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.
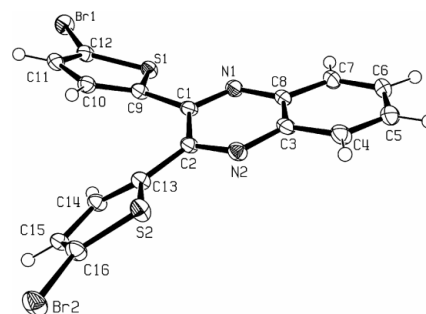
Figure 1
A view of (I). Displacement ellipsoids are drawn at the 50% probability level.

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