

Bis(4-propargyloxy-3-quinolylthio)-  
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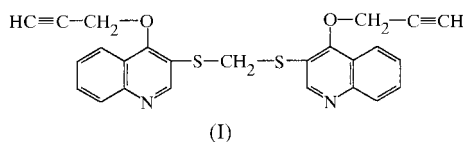
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The molecular structure of the title compound, C<sub>25</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>, in the crystal is characterized by almost parallel quinoline and propargyl groups that point in opposite directions out of the quinoline planes. Intermolecular C≡C–H···N hydrogen bonding is observed, but the hydrogen-bond geometry is poor.

## Comment

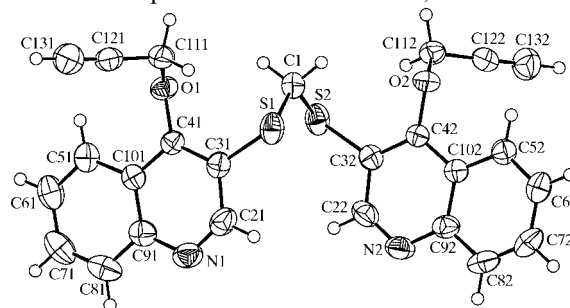
Alkynylquinolines comprise an important class of biologically active compounds which have been considered as bactericides, fungicides and analgesics (Smith, 1950; Blumenthal, 1959; Burckhardt & Zimmermann, 1972). Synthetic methods for preparation of alkynylquinolines are of interest with regard to the synthesis of enediyne antitumour antibiotics or similar structural models (Nicolaou & Dai, 1991; Maier *et al.*, 1999). A simple and efficient method for the synthesis of propargyl thioquinolines by reaction of thioquinanthrene with alkoxides has been reported recently (Boryczka, 1999). Furthermore, the intermolecular interactions of alkynylquinolines may exhibit non-conventional hydrogen-bonding effects. Recently, we have reported the crystal structures of 3-methylthio-4-propargylthioquinoline and two salts of this molecule, and found short C≡C–H···N and C≡C–H···O hydrogen bonds (Boryczka *et al.*, 2000; Boryczka & Steiner, 2000). We have now prepared the larger molecule bis(4-propargyloxy-3-quinolylthio)methane, (I), and report here its molecular and crystal structure.



The molecular structure of (I) is shown in Fig. 1. All bond lengths and angles are normal (relevant values are given in Table 1). The conformation has almost twofold symmetry. The –S–CH<sub>2</sub>–S– link between the quinoline moieties is almost

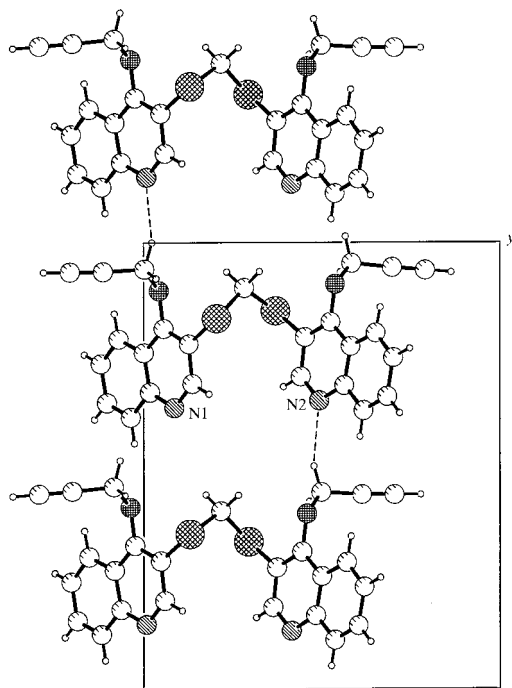
perpendicular to the quinoline planes [torsion angles C21–C31–S1···S2 = –93.8 (2), C22–C32–S2···S1 = –83.1 (2) and C31–S1···S2–C32 = 116.9 (1)°]. The two aromatic planes are roughly parallel with an interplanar angle of 7.9 (1)°. The offset between the thioquinoline planes is 3.067 (1) Å at the S atoms. The intramolecular S···O distances are S1···O1 = 3.189 (1) and O2···S2 = 3.160 (1) Å, respectively. This parallels the molecular structure of bis(4-bromophenylthio)methane (Berthon *et al.*, 1970) and 4-methoxy-3'-methylthio-3,4'-diquinolyl sulfide (Boryczka *et al.*, 1990). Further short intramolecular distances are C111···S1 = 3.291 (2) and C112···S2 = 3.338 (2) Å, associated with C–H···S contacts of H···S = 2.53 and 2.61 Å (for C–H normalized to 1.08 Å) and C–H···S angles of 127 and 124°, respectively. The propargyl groups are pointing out of the quinoline planes (Table 1). The C≡C–H groups are anti-parallel and lie far apart from each other (C131···C132 = 12.529 Å).

In the crystal lattice, the pseudo-twofold axis running through C1 is oriented almost parallel with the crystallographic y axis, and is displaced at C1 by only 0.412 Å from a screw axis of space group *P*2<sub>1</sub>/*n*. This leads to the formation of molecular ribbons as shown in Fig. 2. The displacement of the molecular axis from the crystallographic axis is sufficiently large to generate substantial differences in the intermolecular interactions of the two halves of the molecule. In particular, the pyridyl-N atom N2 accepts a short and linear C–H···N hydrogen bond, whereas N1 does not [C111–H···N2(½ – x, y – ½, ½ – z) with H···N = 2.30, C···N = 3.327 (3) Å, angle = 158°, for normalized C–H]. The lateral interactions of the molecular ribbons are dominated by aromatic stacking. The two C≡C–H groups are involved only in hydrogen bonds of poor geometries directed at N atoms of neighbouring ribbons [C131–H···N1(½ + x, ½ – y, ½ + z) and C132–H···N2(–½ + x, ½ – y, –½ + z) with H···N = 2.58 and 2.71 Å, and angles of 135 and 131°, respectively]. For comparison, the C≡C–H···N hydrogen bond in 3-methylthio-4-propargylthioquinoline has an H···N distance of 2.28 Å (Boryczka *et al.*, 2000), and in a set of 12 C≡C–H···N hydrogen bonds in terminal alkynes, a mean distance of H···N = 2.40 Å has been found (Steiner, 1998; also see Desiraju & Steiner, 1999). This means that in the present compound, the most favourable C–H···N hydrogen bond is not donated by the most acidic C–H group, but by a less activated one. We assume that this circumstance is due to the awkward shape of the molecule that, unlike the much



**Figure 1**  
The molecular structure of (I), showing 30% probability displacement ellipsoids.

simpler 3-methylthio-4-propargylthioquinoline, does not allow efficient crystal packing and favourable hydrogen bonding at the same time.



**Figure 2**  
The molecular ribbon of (I), projected on the  $yz$  plane;  $\text{C}\equiv\text{C}-\text{H}\cdots\text{N}$  hydrogen bonds are indicated by dashed lines. N atoms are shaded with diagonal lines, and O and S atoms with grids (S atoms are drawn with a larger diameter than O atoms).

## Experimental

Bis(4-propargyloxy-3-quinolythio)methane, (I), was prepared following published procedures (Boryczka, 1999) and crystallized from ethanol.  $^1\text{H}$  NMR and MS spectral data have also been given by Boryczka (1999).

### Crystal data

$\text{C}_{25}\text{H}_{18}\text{N}_2\text{O}_2\text{S}_2$

$M_r = 442.53$

Monoclinic,  $P2_1/n$

$a = 10.7358$  (10) Å

$b = 15.8301$  (12) Å

$c = 13.4377$  (8) Å

$\beta = 110.482$  (6)°

$V = 2139.3$  (3) Å<sup>3</sup>

$Z = 4$

$D_x = 1.374$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

Cell parameters from 50 reflections

$\theta = 4.2\text{--}18.2^\circ$

$\mu = 0.274$  mm<sup>-1</sup>

$T = 293$  K

Block, yellow

$0.30 \times 0.23 \times 0.18$  mm

### Data collection

Nonius KappaCCD diffractometer

$\omega$  scans

11 444 measured reflections

4887 independent reflections

3692 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\text{max}} = 27.50^\circ$

$h = -12 \rightarrow 13$

$k = -20 \rightarrow 16$

$l = -17 \rightarrow 13$

### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.048$

$wR(F^2) = 0.105$

$S = 1.104$

4887 reflections

298 parameters

Only H-atom displacement parameters were refined

$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2 + 1.1015P]$

where  $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\text{max}} = 0.23$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.24$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

S1—C31	1.770 (2)	N1—C91	1.373 (3)
S1—C1	1.805 (2)	C121—C131	1.166 (3)
S2—C32	1.770 (2)	N2—C22	1.312 (3)
S2—C1	1.808 (2)	N2—C92	1.372 (3)
N1—C21	1.316 (3)	C122—C132	1.170 (3)
C31—S1—C1	103.04 (9)	C21—N1—C91	116.69 (19)
C32—S2—C1	101.18 (9)	C22—N2—C92	116.94 (18)
C41—O1—C111	117.56 (14)	S1—C1—S2	116.18 (12)
C42—O2—C112	116.70 (14)	C1—S1—C31—C21	-121.6 (2)
C1—S1—C31—C21	-121.6 (2)	C112—O2—C42—C32	68.2 (2)
C111—O1—C41—C31	63.4 (2)	C42—O2—C112—C122	78.5 (2)
C41—O1—C111—C121	81.5 (2)	C31—S1—C1—S2	61.7 (1)
C1—S2—C32—C22	-110.1 (2)	C32—S2—C1—S1	58.9 (1)

H atoms bonded to carbon were treated as riding using the default parameter at room temperature  $\text{C}-\text{H} = 0.93$  Å and with isotropic displacement parameters allowed to vary. All H-atom displacement parameters refined to realistic values in the range 0.045–0.096 Å<sup>2</sup>.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1140). Services for accessing these data are described at the back of the journal.

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