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C≡C—H···N hydrogen bonding in 3-methylthio-4-propargylthioquinoline

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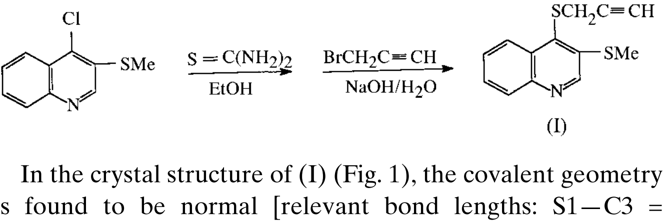
The title compound, $C_{13}H_{11}NS_2$, contains a C≡C—H···N hydrogen bond to a pyridine-type N atom, with a C···N distance of 3.305 (4) Å and an H···N distance of 2.28 Å. This is one of the shortest C—H···N hydrogen bonds known.

Comment

We are studying acetylenic derivatives of thioquinolines as a new series of compounds which can be efficiently obtained from reactions of thioquinanthrene with alkoxides (Boryczka, 1999). Apart from the synthetic chemical interest, the title compound, (I), is of relevance in the context of intermolecular interactions. The terminal alkyne group is expected to form a C≡C—H···*X* hydrogen bond, with *X* being one of the potential hydrogen-bond acceptors of the molecule. This could be the N atom, but also the π systems of the benzyl group, the pyridine moiety and the C≡C bond (Desiraju & Steiner, 1999). The divalent S atoms in the configuration C—S—C are more or less non-polar and are not expected to accept a hydrogen bond from C≡C—H (see Allen *et al.*, 1997). Which of the relevant groups will actually form a hydrogen bond in the crystal cannot be predicted.



(I)

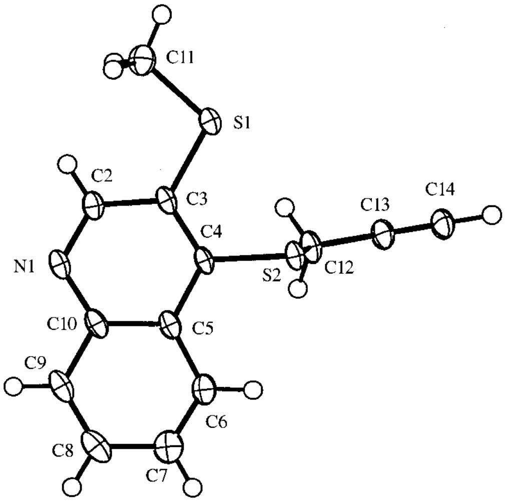


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

In the crystal structure of (I) (Fig. 1), the covalent geometry is found to be normal [relevant bond lengths: S1—C3 = 1.759 (3), S1—C11 = 1.808 (3), C2—C4 = 1.775 (2), S2—C12 = 1.825 (3) and C13≡C14 = 1.181 (4) Å; angles at the S atoms: 103.8 (1)° at S1 and 99.2 (1)° at S2] and is almost the same as in 3,4-dimethylthioquinoline (Maślankiewicz *et al.*, 1991). The methyl group at S1 is almost exactly in the quinoline plane [C2—C3—S1—C11 = 0.7 (3)°]. At S2, the S2—C12 bond involving the propynyl group is rotated perpendicularly out of the quinoline plane [C3—C4—S2—C12 = −86.9 (2)°] and the propargyl group itself is then oriented parallel to the C4—S2 bond [C4—S2—C12—C13 = 173.5 (2)°]. A similar situation occurs in 3,4-dimethylthioquinoline (Maślankiewicz *et al.*, 1991).

In the crystal, layers are formed in which neighbouring molecules are related by translation only (Fig. 2). The inversion-related molecules form separate layers. The C≡C—H group forms a clear hydrogen bond with the N atom of a neighbouring molecule at (x, $y - 1$, $z - 1$), with C···N = 3.305 (4) Å. The interaction is directed towards the electron lone pair of N. If the C—H bond is normalized to 1.08 Å, an

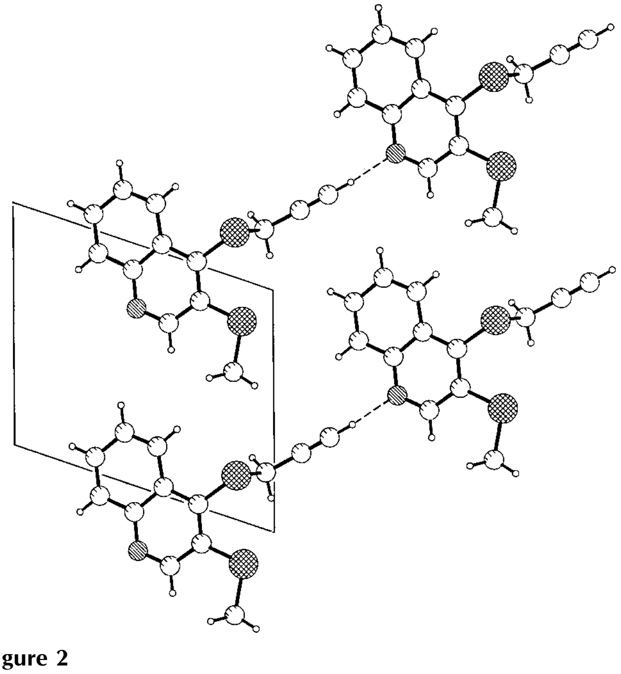


Figure 2
The crystal packing of (I). C≡C—H···N hydrogen bonds are indicated by dashed lines.

H$\cdots$N distance of 2.28 Å and a C—H$\cdots$N angle of 157° are obtained. This is a very short distance for a C—H$\cdots$N hydrogen bond (Mascal, 1998); for hydrogen bonds from the acidic C—H donors in C≡C—H and $CHCl_3$ to N acceptors, the mean H$\cdots$N distances are reported to be 2.40 and 2.34 Å, respectively (Steiner, 1998). Only a few C≡C—H$\cdots$N interactions have been found shorter than in (I) (Kumar *et al.*, 1998); a classical example is cyanoacetylene with H$\cdots$N = 2.21 and C$\cdots$N = 3.29 Å (Shallcross & Carpenter, 1958). Reasons for the short H$\cdots$N distance in (I) might be the high basicity of the pyridyl N atom and the lack of competition with other hydrogen bonds.

Experimental

The title compound, (I), was synthesized by reaction of 4-chloro-3-methylthioquinoline [obtained following procedures described by Maślankiewicz & Boryczka (1993)] with thiourea, as shown in the scheme above. A mixture of 4-chloro-3-methylthioquinoline (0.42 g, 2.4 mmol), thiourea (0.18 g, 2.4 mmol) and 99.8% ethanol (8 ml) was stirred at 313–318 K for 30 min and then cooled to room temperature. The reaction mixture containing the isothiuronium salt was poured into 20 ml of 5% aqueous sodium hydroxide. Propargyl bromide (0.29 g, 2.4 mmol) was added dropwise to the aqueous layer and the mixture was stirred for 15 min. The resultant solid was filtered off and air-dried to give a crude product, which was then crystallized from benzene–hexane to give 0.4 g (82%) of (I) with m.p. 375–376 K. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.07 (*t*, J = 2.5 Hz, 1H, CH), 2.67 (*s*, 3H, SCH_3), 3.69 (*d*, J = 2.5 Hz, 2H, SCH_2), 7.59–7.69 (*m*, 2H, H-6 and H-7), 8.05–8.08 (*m*, 1H, H-8), 8.54–8.58 (*m*, 1H, H-5), 8.79 (*s*, 1H, H-2) (in the NMR spectrum, we applied systematic atom numbering according to IUPAC rules). MS EI (70 eV) *m*/*z* (relative intensity): 245 (M^+, 25.6), 230 ($M - CH_3$, 100). The melting point was determined on a Buchi 510 capillary apparatus. The ^{1}H NMR spectrum was recorded on a Bruker 300 MSL instrument at 300 MHz. The mass spectrum was obtained on an LKB GC 2091 spectrometer at 70 eV.

Crystal data

$C_{13}H_{11}NS_2$
$M_r = 245.35$
Triclinic, $P\bar{1}$
$a = 7.448$ (3) Å
$b = 8.514$ (3) Å
$c = 9.786$ (3) Å
$\alpha = 107.57$ (3)°
$\beta = 100.99$ (3)°
$\gamma = 94.57$ (3)°
$V = 574.4$ (4) Å^3
$Z = 2$
$D_x = 1.418$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 37 reflections
$\theta = 3.8$–18.0°
$\mu = 0.432$ mm^{-1}
$T = 125$ K
Block, yellow
0.25 × 0.20 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
3618 measured reflections
2616 independent reflections
2315 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0363$
$\theta_{max} = 27.50°$
$h = -9 \rightarrow 7$
$k = -11 \rightarrow 10$
$l = -12 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.127$
$S = 1.098$
2616 reflections
157 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 1.3190P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.930$ e Å^{-3}
$\Delta\rho_{min} = -0.464$ e Å^{-3}

H atoms bonded to C were treated as riding using default parameters for C—H bond lengths at the temperature of measurement, with isotropic displacement parameters allowed to vary. The methyl groups were allowed to rotate. All H-atom displacement parameters refined to realistic values, in the range 0.021–0.065 Å^2. By far the highest difference electron-density peak is located 0.86 Å from S2. All attempts to refine disorder that could lead to this peak failed.

Data collection: *EVAL*14 (Duisenberg, 1998). Cell refinement: *EVAL*14. Data reduction: *EVAL*14. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1986). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Software used to prepare material for publication: *SHELXL*97, *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1124). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Bird, C. M., Rowland, R. S. & Raithby, P. R. (1997). *Acta Cryst.* B**53**, 696–701.
Boryczka, S. (1999). *Heterocycles*, **51**, 631–637.
Desiraju, G. R. & Steiner, T. (1999). In *The Weak Hydrogen Bond in Structural Chemistry and Biology*. Oxford University Press.
Duisenberg, A. J. M. (1998). Thesis, Utrecht University, The Netherlands.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kumar, S., Subramanian, K., Srinivasan, R., Rajagopalan, K. & Steiner, T. (1998). *J. Mol. Struct.* **471**, 251–255.
Mascal, M. (1998). *Chem. Commun.* pp. 303–304.
Maślankiewicz, A. & Boryczka, S. (1993). *J. Heterocycl. Chem.* **30**, 1623–1628.
Maślankiewicz, A., Wyszomirski, M., Głowiak, T. & Gogol, A. (1991). *J. Crystallogr. Spectrosc. Res.* **21**, 559–565.
Shallcross, F. V. & Carpenter, G. B. (1958). *Acta Cryst.* **11**, 490–496.
Sheldrick, G. M. (1986). *SHELXS*86. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Steiner, T. (1998). *New J. Chem.* **22**, 1099–1103.

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