Hydrogen bonding in two salts of 3-methylthio-4-(propargylthio)-quinoline

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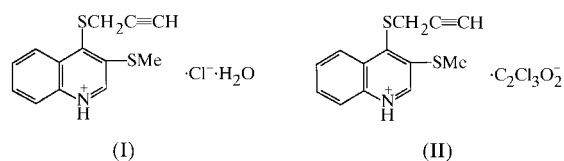Correspondence e-mail: steiner@chemie.fu-berlin.de

In 3-methylthio-4-(propargylthio)quinolinium chloride monohydrate, $C_{13}H_{12}NS_2^+ \cdot Cl^- \cdot H_2O$, and 3-methylthio-4-(propargyl-thio)quinolinium trichloroacetate, $C_{13}H_{12}NS_2^+ \cdot C_2Cl_3O_2^-$, the terminal alkyne group forms $C \equiv C—H \cdots O$ hydrogen bonds of favourable geometry. The conformation of the flexible propargylthio group is different in the two structures.

Comment

Acetylenic derivatives of thioquinolines are of synthetic chemical interest (Boryczka, 1999) and are also of interest in the context of hydrogen bonding. In particular, the terminal alkyne group can form a variety of directional intermolecular interactions, many of which have not yet been fully explored (Desiraju & Steiner, 1999). Recently, we have communicated the crystal structure of 3-methylthio-4-(propargylthio)-quinoline, (I), which contains an unusually short $C \equiv C—H \cdots N$ hydrogen bond with an $H \cdots N$ distance of 2.28 Å (Boryczka et al., 2000). In order to study the intermolecular interactions of the propargyl group of this molecule in

different environments and different competitive situations, we have prepared the chloride and trichloroacetate salts of (I), namely, 3-methylthio-4-propargylthioquinolinium chloride monohydrate, (II), and 3-methylthio-4-propargylthioquinolinium trichloroacetate, (III). It is also of interest to investigate to which degree the conformation of (I) responds to salt formation and variation of the intermolecular environment. The results of these studies are presented here.

The molecular structure of (II) is shown in Fig. 1. The overall conformation of the cation is very similar to that in the
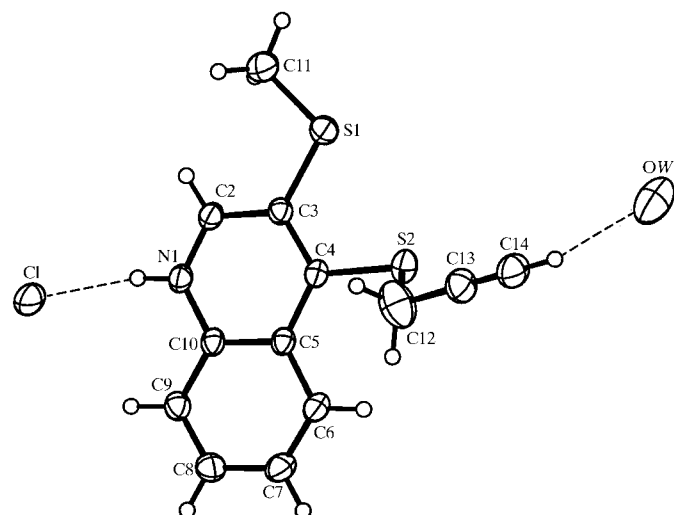

Figure 1
The molecular structure of (II), showing 30% probability displacement ellipsoids. The quinoline plane is drawn tilted by 10° from the plane of the paper around a vertical axis; hydrogen bonds are indicated by dashed lines.

uncharged parent compound; relevant torsion angles are given in Table 1. As expected, the protonated pyridyl-N atom is engaged in an $N—H \cdots Cl^-$ hydrogen bond. The $N^+ \cdots Cl^-$ distance of 3.030 (3) Å is typical for this kind of interaction (Steiner, 1998). The C2—N1—C10 angle of 123.7 (2)° is significantly widened from 120°, which is a normal consequence of pyridyl protonation. In the uncharged molecule, (I), for comparison, the C—N—C angle is 118.5 (2)°.

The propargyl group of (II) donates a $C \equiv C—H \cdots O$ hydrogen bond to the water molecule, with a $C \cdots O$ distance of 3.352 (6) Å. If the C—H distance is normalized to 1.08 Å, a hydrogen-bond geometry of $H \cdots O = 2.29$ Å and $C—H \cdots O =$
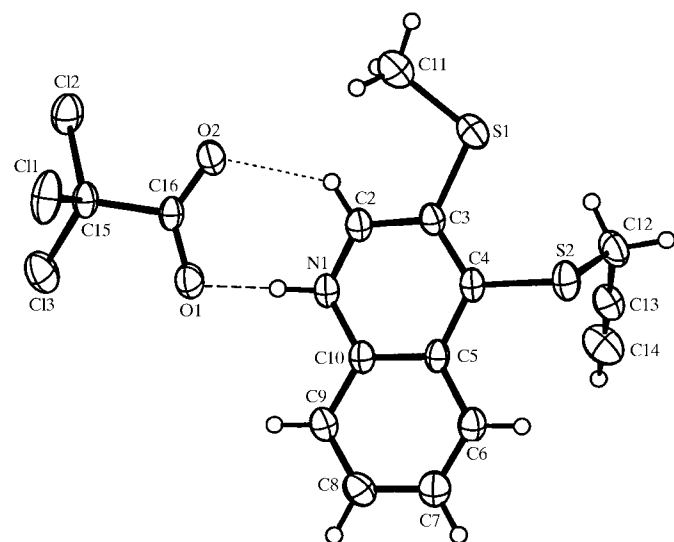

Figure 2
The molecular structure of (III), showing 30% probability displacement ellipsoids. The quinoline plane is drawn tilted by 10° from the plane of the paper around a vertical axis; hydrogen bonds are indicated by dashed lines.

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166° is obtained. This can be considered as quite a favourable geometry (Desiraju & Steiner, 1999). It is unfortunate that the water molecule shows clear signs of disorder: the displacement ellipsoid is highly anisotropic and H-atom positions cannot be located. In consequence, the water hydrogen-bond interactions cannot be fully assigned.

The shortest intermolecular contacts are to chloride ions, $OW \cdots Cl(x, y-1, z+1) = 3.321\,(5)$ Å and $OW \cdots Cl(1-x, 1-y, 2-z) = 3.237\,(5)$ Å, both of which are indicative of $OW-H \cdots Cl^-$ hydrogen bonds. The next shortest contact is to a symmetry-related water molecule, with $OW \cdots OW(-x, -y, 3-z) = 3.338\,(9)$ Å, which very probably does not represent a hydrogen bond (both water-H atoms are presumably directed towards Cl^- ions).

The molecular structure of the trichloroacetate salt, (III), is shown in Fig. 2. Similar to (II), protonation of N1 leads to widening of the C—N—C angle to 122.7 (3)°. N1—H forms a short $N-H \cdots O$ hydrogen bond to the anion, with $N1 \cdots O1$ being only 2.573 (4) Å. The other O atom of the anion is involved in a $C-H \cdots O$ bond donated by C2—H [$C2 \cdots O2 = 3.076\,(4)$ Å and $H2 \cdots O2 = 2.22$ Å, and $C2-H \cdots O2 = 131°$ for C2—H normalized to 1.08 Å]. This hydrogen-bond pattern, i.e. the formation of a pair of $N-H \cdots O$ and $C-H \cdots O$ interactions, frequently occurs when carboxylate ions bind to pyridinium groups.

The propargyl group of (III) has a different orientation to that observed in (I) and (II). It projects out of the quinoline plane and donates a hydrogen bond to a trichloroacetate ion that is placed roughly 'above' the quinoline moiety [Fig. 3; $C13 \equiv C14-H \cdots O2(x-\frac{1}{2}, y-\frac{1}{2}, z)$: $C \cdots O = 3.205\,(6)$ Å and $H \cdots O = 2.26$ Å, and $C-H \cdots O = 151°$, for C—H normalized to 1.08 Å].

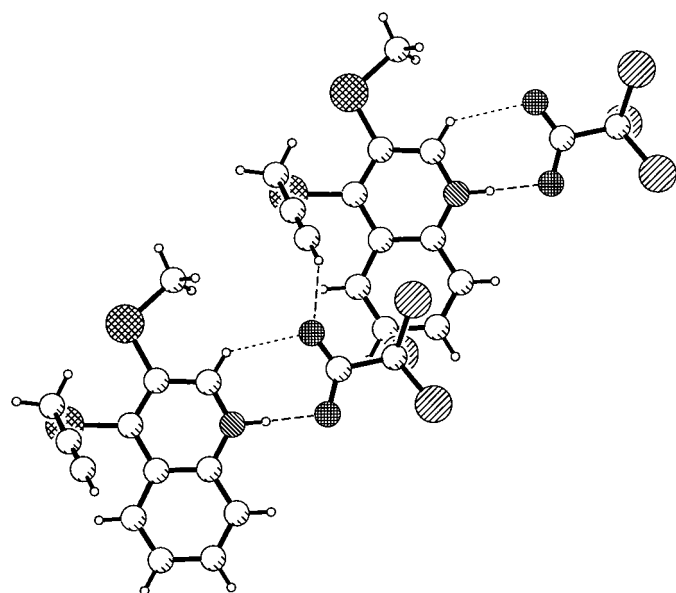In both these salts of 3-methylthio-4-(propargylthio)-quinoline, we find favourable $C \equiv C-H \cdots O$ interactions of the propargyl group. This shows once again that the terminal alkyne group is a sufficiently strong donor to compete successfully for acceptors even if O—H and N—H donors are present (see also the structure of 1-ethynylcyclohexyl-ammonium acetate; Steiner et al., 1999).

Experimental

The preparation of 3-methylthio-4-(propargylthio)quinoline, (I), has been reported previously by Boryczka et al. (2000). Crystals of the chloride monohydrate salt, (II), were obtained by slow evaporation of an MeOH/H₂O/HCl solution of (I). Crystals of the trichloroacetate salt, (III), were obtained by slow evaporation of an equimolar solution of (I) and trichloroacetic acid in MeOH.

Compound (II)

Crystal data

$C_{13}H_{12}NS_2{}^+ \cdot Cl^- \cdot H_2O$	$Z = 2$
$M_r = 299.85$	$D_x = 1.428$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.571\,(4)$ Å	Cell parameters from 39
$b = 9.486\,(6)$ Å	reflections
$c = 10.528\,(4)$ Å	$\theta = 5.1–16.2°$
$\alpha = 85.72\,(4)°$	$\mu = 0.560$ mm^{-1}
$\beta = 71.16\,(4)°$	$T = 293$ K
$\gamma = 76.94\,(5)°$	Needle, yellow
$V = 697.1\,(6)$ Å^3	$0.65 \times 0.10 \times 0.05$ mm

Data collection

Stoe four-circle diffractometer	$h = -6 \rightarrow 9$
ω scans	$k = -12 \rightarrow 12$
3330 measured reflections	$l = -9 \rightarrow 13$
3149 independent reflections	3 standard reflections
2429 reflections with $I > 2\sigma(I)$	frequency: 90 min
$R_{int} = 0.035$	intensity decay: 4%
$\theta_{max} = 27.51°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0789P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.051$	$+ 0.2963P]$
$wR(F^2) = 0.146$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.018$	$(\Delta/\sigma)_{max} = 0.001$
3149 reflections	$\Delta\rho_{max} = 0.46$ e Å^{-3}
179 parameters	$\Delta\rho_{min} = -0.28$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °) for (II).

S1—C3	1.753 (3)	N1—C2	1.319 (3)
S1—C11	1.786 (3)	N1—C10	1.355 (3)
S2—C4	1.760 (3)	N1—H1	0.88 (4)
S2—C12	1.796 (4)	C13—C14	1.159 (4)
C3—S1—C11	103.84 (14)	C2—C3—S1	122.3 (2)
C4—S2—C12	101.79 (16)	C3—C4—S2	117.91 (19)
C2—N1—C10	123.7 (2)	C5—C4—S2	121.89 (19)
C4—C3—S1	119.23 (19)		
C11—S1—C3—C2	−5.6 (3)	C12—S2—C4—C3	116.8 (3)
S1—C3—C4—S2	−0.2 (3)	C4—S2—C12—C13	−165.5 (3)

Figure 3
The crystal packing of (III); hydrogen bonds are indicated by dashed lines.

Table 2
Selected geometric parameters (Å, °) for (III).

S1—C3	1.747 (4)	N1—C10	1.351 (4)
S1—C11	1.773 (5)	N1—H1	0.91 (5)
S2—C4	1.764 (3)	C13—C14	1.154 (6)
S2—C12	1.825 (4)	O1—C16	1.249 (4)
N1—C2	1.312 (5)	O2—C16	1.219 (4)
C3—S1—C11	103.5 (2)	C3—C4—S2	119.8 (3)
C4—S2—C12	100.27 (19)	C5—C4—S2	120.3 (3)
C2—N1—C10	122.7 (3)	O2—C16—C15	116.5 (3)
C4—C3—S1	120.9 (3)	O1—C16—C15	114.9 (3)
C2—C3—S1	120.9 (3)		
C11—S1—C3—C2	11.7 (4)	C4—S2—C12—C13	−63.8 (4)
S1—C3—C4—S2	−0.6 (4)	Cl1—C15—C16—O1	86.0 (3)
C12—S2—C4—C3	−75.1 (3)		

Compound (III)

Crystal data

$C_{13}H_{12}NS_2^+ \cdot C_2Cl_3O_2^-$
$M_r = 408.73$
Monoclinic, $C2/c$
$a = 19.430\ (11)$ Å
$b = 5.338\ (3)$ Å
$c = 36.66\ (3)$ Å
$\beta = 111.67\ (5)°$
$V = 3533\ (4)$ Å^3
$Z = 8$

$D_x = 1.537$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26
  reflections
$\theta = 5.0–15.1°$
$\mu = 0.761$ mm^{-1}
$T = 293\ (2)$ K
Needle, yellow
$1.2 \times 0.10 \times 0.05$ mm

Data collection

Stoe four-circle diffractometer
ω scans
4098 measured reflections
4031 independent reflections
2781 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.54°$

$h = -24 \rightarrow 24$
$k = -6 \rightarrow 2$
$l = -42 \rightarrow 47$
3 standard reflections
  frequency: 90 min
  intensity decay: 6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.165$
$S = 1.011$
4031 reflections
224 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0764P)^2 + 5.2477P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}

H atoms bonded to C atoms were treated using a riding model (C—H 0.93–0.97 Å), with the default parameters set at C—H bond lengths at room temperature and with isotropic displacement parameters allowed to vary. The methyl groups were allowed to rotate. The water-H atoms in (II) could not be located unambiguously and are not included in the structure model. The apparent disorder of the water molecule could not be resolved. The H atoms bonded to N atoms were located in difference Fourier calculations and refined isotropically, with U_{eq} values of 0.059 (9) and 0.066 (13) Å^2 in (II) and (III), respectively.

For both compounds, data collection: Stoe diffractometer software; cell refinement: Stoe diffractometer software; data reduction: Stoe diffractometer software; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL*97.

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