

## Quinoline-2(1*H*)-thione, a structure with $Z' = 8$

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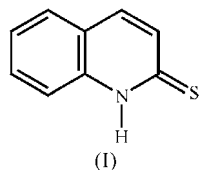
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The title compound, C<sub>9</sub>H<sub>7</sub>NS, crystallizes as the thione tautomer with  $Z' = 8$  (four independent dimers with local inversion symmetry *via* two N—H···S=C hydrogen-bond systems). The dimers are arranged in chains parallel to  $[\bar{1}10]$ , each chain being crystallographically independent. These chains are associated into layers *via* stacking of ring systems. The  $Z'$  value can be rationalized in terms of a factor 2 for dimer formation without crystallographic symmetry and an additional factor 4 for differing stacking environments.

### Comment

We are interested in the structures and optical properties of formal ‘mercaptans’ of aromatic N-heterocycles, in which, however, the usual tautomer is the thione form, with a double bond to the S atom and a protonated N atom. We have published studies of 2-mercaptothiazoline (thiazoline-2-thione; Flakus, Tyl & Jones, 2002) and 4-mercaptopyridine (pyridine-4-thione; Flakus, Miros & Jones, 2002); the former consists of inversion-symmetric dimers, hydrogen bonded by N—H···S=C systems, whereas the latter forms zigzag chains,



also *via* N—H···S=C hydrogen bonds. Pyridine-2-thione (Reynolds *et al.*, 1995) also forms inversion-symmetric dimers, and it has found use as a ligand in transition metal chemistry (Reynolds *et al.*, 1995; Usón *et al.*, 1990).

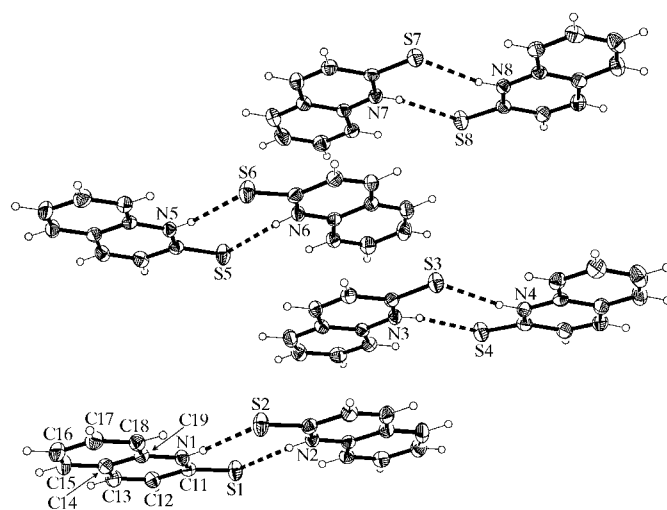
We report here the structure of quinoline-2(1*H*)-thione, (I), an important reagent in analytical chemistry (Karagiannidis *et al.*, 1990; Paneli & Voulgaropoulos, 1991; Steed & Tocher, 1992; Leeaphon *et al.*, 1993; Kitagawa *et al.*, 1993; Aslanidis *et al.*, 1998). Solution IR spectra (Flakus, 1994) indicated the presence of inversion-symmetric hydrogen-bonded dimers. Both the thione and the mercaptan forms have been found

in low-temperature matrices by IR spectroscopy (Prusinowska *et al.*, 1995).

The structure determination of (I) establishes the presence of the expected thione form of the molecule, but the most striking feature is the presence of eight independent molecules (Fig. 1). The Cambridge Structural Database (CSD, Version of July 2004; Allen, 2002) contains only 61 hits with  $Z' \geq 8$ , out of a total of 322 421 entries. We can see no evidence that unrecognized twinning or structure modulation has led to an inappropriate cell, and a variety of programs have failed to indicate any overlooked symmetry. Together with the Flack parameter (Flack, 1983) of 0.03 (3), this is good evidence for the absence of a global inversion centre, despite the rather high mean ( $E^2 - 1$ ) value of 0.869.

All eight molecules of (I) are closely similar and essentially planar (all mean deviations of non-H atoms from planarity are less than 0.03 Å). The molecular dimensions may be regarded as normal, *e.g.* the short N—C1 and longer N—C9 bonds, the short C2—C3 and long C3—C4 bonds consistent with the thione tautomer, the C=S bond lengths, and the widened angle at the N atom typical of protonated pyridine systems (Table 1). Note that the numbering is chosen to allow an easy comparison of the independent molecules (the first digit of each atom label is the molecule number) and does not correspond to the IUPAC numbering. Rigid-body libration corrections (Schomaker & Trueblood, 1968) can be applied successfully because of the lack of torsional degrees of freedom, and lie in the range 0.002–0.005 Å (Table 3).

The molecules form the expected inversion-symmetric pairs *via* N—H···S hydrogen bonding (Fig. 1 and Table 2), although the symmetry is only approximate rather than exact. Thus, the ring systems within each pair are not exactly parallel [interplanar angles: molecule 1/molecule 2 = 2.54 (6)°, 3/4 =

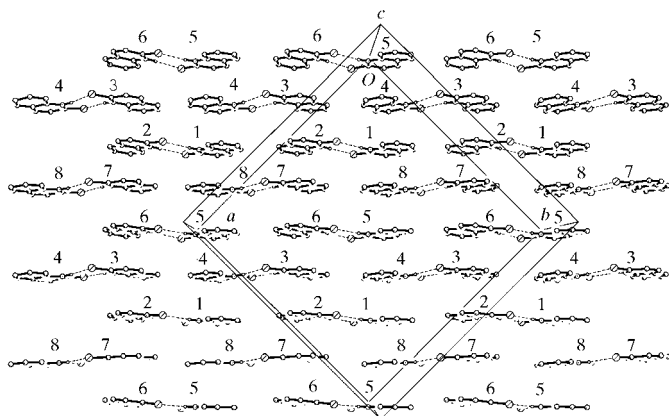


**Figure 1**

The asymmetric unit of (I) in the crystal. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines represent hydrogen bonds. The complete numbering of molecule 1 (bottom left) is given; the numbering of the other molecules can be completed analogously.

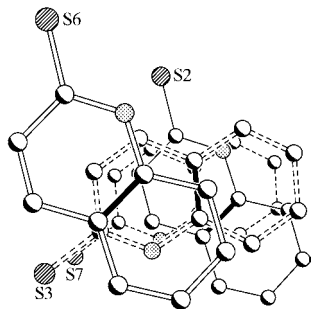
6.51 (6)°, 5/6 = 6.17 (6)°, and 7/8 = 1.45 (6)°, with planes calculated through all non-H atoms]. The H···S=C angles are in the range 109.7 (5)–111.5 (5)°. Each H atom at C8 is forced into proximity with the S atom of the hydrogen-bonded partner, but these contacts (one of which is given as an example in Table 2) should not necessarily be regarded as hydrogen bonds. Similarly, the other C—H···S contacts given for completeness in Table 2 may not be of great structural significance.

The extended packing in the region  $z \simeq 0$  involves chains of hydrogen-bonded pairs parallel to  $[\bar{1}10]$  (Fig. 2), or to  $[110]$  in the region  $z \simeq \frac{1}{2}$ . Each chain consists of only one type of pair, e.g. only molecules 1 and 2. The chains lie in common layers in which only translational symmetry is involved. In Fig. 2, successive pairs in the chain are related by the  $C$ -centring operator ( $x - \frac{1}{2}, \frac{1}{2} + y, z$ ), while the operator ( $\frac{1}{2} + x, \frac{1}{2} + y, z$ ) transforms one chain into its counterpart four chains lower.



**Figure 2**

The packing of (I) in the crystal. H atoms (except those involved in hydrogen bonding) have been omitted for clarity. The view direction is approximately parallel to the  $c$  axis; the region at  $z \simeq 0$  is shown. The molecules are numbered 1–8. The untransformed molecules of the asymmetric unit lie in the alternative layer at  $z = \frac{1}{2}$  (see *Comment*).



**Figure 3**

The stacking of molecules of (I) in the crystal. H atoms have been omitted for clarity. This is the stack involving molecules 6 (bonds as solid double lines), 3 (broken double lines), 2 (solid single lines) and 7 (broken single lines), in that order from top to bottom. The central C4—C9 bonds are drawn as thick solid bonds to emphasize their positions with respect to the neighbouring pyridine rings (see text); that of molecule 7 is eclipsed. The view direction is perpendicular to the best plane of molecule 3.

The current interest in crystal packing and ‘engineering’ extends to structures with high  $Z'$  [see, for example, Steed (2003), and references therein]. Why should such effects arise? There seems, at first, to be little reason why compound (I) should have  $Z' = 8$ , when its smaller analogue pyridine-2-thione has  $Z' = 1$  (Reynolds *et al.*, 1995), although the lack of global symmetry in the hydrogen-bonded pairs could easily lead to  $Z' = 2$ . A rationalization may be sought in the stacking geometry within the layers of (I). As can be seen from Fig. 1, molecules 2, 3, 6 and 7 (with coordinates as chosen for the asymmetric unit) are stacked above each other. This is confirmed in Fig. 2, which shows two stacks, the second being composed of molecules 1, 4, 5 and 8, in that order. All the rings are approximately parallel (no interplanar angles  $> 10^\circ$ ), but are offset, as is expected for stable packing (Hunter & Sanders, 1990). The offsetting is such that the central C4—C9 bond, common to both rings, lies above the centre of the pyridine ring of the neighbouring molecule in the stack. However, a closer inspection shows that the molecules thereby acquire different environments. If we denote the interaction of C4—C9 lying over the ring centre as  $\rightarrow$ , then the four independent interactions in one stack are: molecule 7  $\rightarrow$  molecule 6  $\rightarrow$  molecule 3  $\rightarrow$  molecule 2  $\leftarrow$  molecule 7' (generated by stack translation). This can be seen in Fig. 3. Thus, the stacking is such that there are three interactions in one direction, but the fourth is in the opposite direction. This explains the factor 4 that changes  $Z'$  from 2 to 8. In the second independent stack, the interactions are analogous: molecule 1  $\rightarrow$  molecule 4  $\rightarrow$  molecule 5  $\rightarrow$  molecule 8  $\leftarrow$  molecule 1'.

Thus one can, at least phenomenologically, explain the  $Z'$  value for (I), although it would presumably be impossible, given the current state of knowledge, to predict the packing or explain the detailed causes. It would clearly be a worthwhile exercise to attempt to grow crystals of alternative polymorphs of (I), but in our hands the compound was most unwilling to crystallize adequately from any solvent.

## Experimental

Compound (I) was prepared according to the method of Rosenhauer *et al.* (1929), but is now commercially available from Aldrich. Crystals of (I) were grown by slow evaporation of ethanol solutions, although good single crystals were extremely rare.

### Crystal data

$C_9H_7NS$   
 $M_r = 161.22$   
 Monoclinic,  $Cc$   
 $a = 19.9772$  (14) Å  
 $b = 19.9588$  (14) Å  
 $c = 15.6622$  (11) Å  
 $\beta = 93.014$  (4)°  
 $V = 6236.2$  (8) Å<sup>3</sup>  
 $Z = 32$

$D_x = 1.374$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 5773 reflections  
 $\theta = 2.8$ – $29.6^\circ$   
 $\mu = 0.34$  mm<sup>-1</sup>  
 $T = 133$  (2) K  
 Block, brown–yellow  
 $0.28 \times 0.24 \times 0.24$  mm

### Data collection

Bruker SMART 1000 CCD area-detector diffractometer  
 $\omega$  and  $\varphi$  scans  
 44 742 measured reflections  
 15 776 independent reflections  
 12 944 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.034$   
 $\theta_{max} = 28.7^\circ$   
 $h = -26 \rightarrow 26$   
 $k = -26 \rightarrow 26$   
 $l = -20 \rightarrow 20$

## Refinement

Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.034$  $wR(F^2) = 0.078$  $S = 0.96$ 

15 776 reflections

825 parameters

H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.0429P)^2]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$ 

Absolute structure: Flack (1983)

Flack parameter = 0.03 (3)

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

|            |             |            |             |
|------------|-------------|------------|-------------|
| S1—C11     | 1.6856 (19) | S5—C51     | 1.6876 (19) |
| N1—C11     | 1.350 (2)   | N5—C51     | 1.346 (2)   |
| N1—C19     | 1.391 (2)   | N5—C59     | 1.389 (2)   |
| C12—C13    | 1.351 (3)   | C52—C53    | 1.348 (3)   |
| C13—C14    | 1.436 (3)   | C53—C54    | 1.430 (3)   |
| S2—C21     | 1.6892 (19) | S6—C61     | 1.693 (2)   |
| N2—C21     | 1.351 (2)   | N6—C61     | 1.347 (2)   |
| N2—C29     | 1.379 (2)   | N6—C69     | 1.384 (2)   |
| C22—C23    | 1.353 (3)   | C62—C63    | 1.345 (3)   |
| C23—C24    | 1.432 (3)   | C63—C64    | 1.437 (3)   |
| S3—C31     | 1.6887 (19) | S7—C71     | 1.6859 (19) |
| N3—C31     | 1.343 (2)   | N7—C71     | 1.351 (2)   |
| N3—C39     | 1.385 (2)   | N7—C79     | 1.383 (2)   |
| C32—C33    | 1.354 (3)   | C72—C73    | 1.351 (3)   |
| C33—C34    | 1.434 (3)   | C73—C74    | 1.429 (3)   |
| S4—C41     | 1.689 (2)   | S8—C81     | 1.689 (2)   |
| N4—C41     | 1.350 (2)   | N8—C81     | 1.345 (2)   |
| N4—C49     | 1.378 (2)   | N8—C89     | 1.381 (2)   |
| C42—C43    | 1.348 (3)   | C82—C83    | 1.349 (3)   |
| C43—C44    | 1.432 (3)   | C83—C84    | 1.428 (3)   |
| C11—N1—C19 | 124.79 (16) | C51—N5—C59 | 124.93 (16) |
| C21—N2—C29 | 124.91 (16) | C61—N6—C69 | 124.82 (16) |
| C31—N3—C39 | 125.25 (16) | C71—N7—C79 | 124.93 (16) |
| C41—N4—C49 | 125.14 (16) | C81—N8—C89 | 125.18 (16) |

Table 2

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

| D—H...A                     | D—H        | H...A      | D...A       | D—H...A    |
|-----------------------------|------------|------------|-------------|------------|
| N1—H01...S2                 | 0.863 (14) | 2.475 (14) | 3.3345 (17) | 174.2 (19) |
| N2—H02...S1                 | 0.864 (14) | 2.468 (14) | 3.3166 (16) | 167.2 (19) |
| N3—H03...S4                 | 0.874 (13) | 2.456 (14) | 3.3156 (16) | 168.0 (18) |
| N4—H04...S3                 | 0.866 (13) | 2.444 (14) | 3.2898 (16) | 165.8 (18) |
| N5—H05...S6                 | 0.865 (14) | 2.488 (14) | 3.3431 (17) | 169.7 (18) |
| N6—H06...S5                 | 0.867 (14) | 2.461 (15) | 3.3149 (16) | 169 (2)    |
| N7—H07...S8                 | 0.851 (13) | 2.463 (14) | 3.3037 (16) | 169.7 (18) |
| N8—H08...S7                 | 0.888 (14) | 2.434 (14) | 3.3109 (16) | 169 (2)    |
| C18—H18...S2                | 0.95       | 2.98       | 3.768 (2)   | 141        |
| C28—H28...S3 <sup>i</sup>   | 0.95       | 3.05       | 3.701 (2)   | 127        |
| C72—H72...S4 <sup>ii</sup>  | 0.95       | 2.91       | 3.6996 (19) | 142        |
| C12—H12...S7 <sup>i</sup>   | 0.95       | 2.85       | 3.6091 (19) | 138        |
| C26—H26...S7 <sup>iii</sup> | 0.95       | 2.95       | 3.845 (2)   | 157        |

Symmetry codes: (i)  $x, 1 - y, z - \frac{1}{2}$ ; (ii)  $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} + z$ ; (iii)  $\frac{1}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$ .

The H atoms of the NH groups were clearly identified in difference syntheses and refined with N—H distances restrained to be equal (command SADI). Other H atoms were included using a riding model, with C—H bond lengths fixed at 0.95  $\text{\AA}$ , and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The Flack parameter was refined on the basis of 7657 Friedel pairs.

Table 3

Librationally corrected bond lengths ( $\text{\AA}$ ).

| Bond  | Molecule |       |       |       |       |       |       |       |
|-------|----------|-------|-------|-------|-------|-------|-------|-------|
|       | 1        | 2     | 3     | 4     | 5     | 6     | 7     | 8     |
| S=C1  | 1.689    | 1.693 | 1.692 | 1.693 | 1.691 | 1.697 | 1.689 | 1.692 |
| N—C1  | 1.352    | 1.353 | 1.345 | 1.352 | 1.348 | 1.350 | 1.353 | 1.347 |
| C1—C2 | 1.437    | 1.436 | 1.443 | 1.441 | 1.437 | 1.436 | 1.433 | 1.443 |
| C2—C3 | 1.354    | 1.357 | 1.357 | 1.351 | 1.350 | 1.348 | 1.354 | 1.352 |
| C3—C4 | 1.438    | 1.434 | 1.436 | 1.434 | 1.433 | 1.440 | 1.432 | 1.430 |
| C4—C5 | 1.407    | 1.412 | 1.405 | 1.405 | 1.412 | 1.411 | 1.412 | 1.407 |
| C5—C6 | 1.378    | 1.374 | 1.379 | 1.369 | 1.376 | 1.371 | 1.372 | 1.380 |
| C6—C7 | 1.396    | 1.406 | 1.406 | 1.409 | 1.407 | 1.406 | 1.400 | 1.404 |
| C7—C8 | 1.380    | 1.375 | 1.374 | 1.379 | 1.376 | 1.383 | 1.378 | 1.379 |
| N—C9  | 1.393    | 1.382 | 1.387 | 1.381 | 1.392 | 1.387 | 1.385 | 1.383 |
| C4—C9 | 1.406    | 1.409 | 1.411 | 1.415 | 1.408 | 1.408 | 1.408 | 1.416 |
| C8—C9 | 1.400    | 1.408 | 1.401 | 1.403 | 1.402 | 1.401 | 1.403 | 1.405 |

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); 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: BM1582). Services for accessing these data are described at the back of the journal.

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