# Hydrogen-bonded chains of rings in 1-(4-chloroanilinomethyl)-5-(4-chlorophenyl)-1,3,5-triazinane-2-thione and hydrogen-bonded sheets in 1-anilinomethyl-5-phenyl-1,3,5-triazinane-2-thione

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In 1-(4-chloroanilinomethyl)-5-(4-chlorophenyl)-1,3,5-triazinane-2-thione, $C_{16}H_{16}Cl_2N_4S$, there are two independent molecules in the asymmetric unit which form inversion dimers via two weak N—H⋯S hydrogen bonds. The dimers are then linked into $C(9)C(14)$ chains by a C—H⋯S hydrogen bond and a C—H⋯Cl contact. In 1-(anilinomethyl)-5-phenyl-1,3,5-triazinane-2-thione, $C_{16}H_{18}N_4S$, molecules are linked into complex sheets via a combination of N—H⋯S and C—H⋯$\pi$ hydrogen bonds.

## Comment

Heterocyclic compounds containing the thiourea structural unit have been found to have strong bioactivity, such as powerful ectoparasiticidal action (Enders et al., 1979), potent antidiabetic properties (Lenzen & Ahmad, 2001) and anti-HIV activity (Lam et al., 1994; Acharya et al., 2001). In addition, some of these compounds can serve as calcium channel blockers, antihypertensive agents and $\alpha$-1a-antagonists (Atwal et al. 1990). Therefore, it is not surprising that the search for new methods to synthesize heterocyclic compounds starting from thiourea has received special attention. Burke and Petersen provided early reports of synthetic studies of 5-alkyl- or 4,6-dialkyl-substituted 1,3,5-triazinane-2-thiones (Burke, 1947; Petersen, 1973). In our development of new routes to diversely substituted 1,3,5-triazinane-2-thiones, several novel 1,5-disubstituted 1,3,5-triazinane-2-thiones have been synthesized by a one-pot three-component condensation of thiourea, aniline and formaldehyde (Zhang et al., 2008). We report here the molecular and supramolecular structures of two such compounds, namely 1-(4-chloroanilinomethyl)-5-(4-chlorophenyl)-1,3,5-triazinane-2-thione, (I), and 1-anil-

inomethyl-5-phenyl-1,3,5-triazinane-2-thione, (II) (Figs. 1 and 2, respectively).

Compound (I) crystallizes with $Z' = 2$ in the $P2_1$ space group and the molecular geometries of the two independent molecules, (Ia) and (Ib) (Fig. 1), are very similar. The triazinane-2-thione rings adopt envelope conformations; atoms N1 and N5
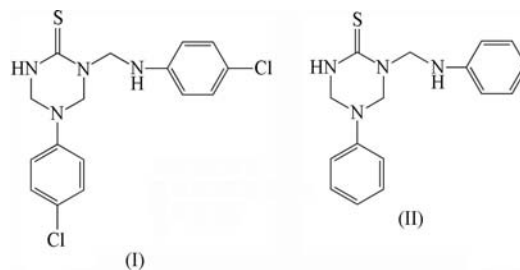


are the flap atoms, displaced by 0.652 and 0.665 Å, respectively, from the planes of the other five atoms. The conformations of the two heterocyclic structural units and the coplanarity of the S1/C9/N2/N3/C7/C8 and S2/C24/N6/N7/C23/C25 fragments in (Ia) and (Ib) are similar to the situation found in other cyclic thiones (Zhang, Zhang et al., 2007; Pavlović et al., 2000).
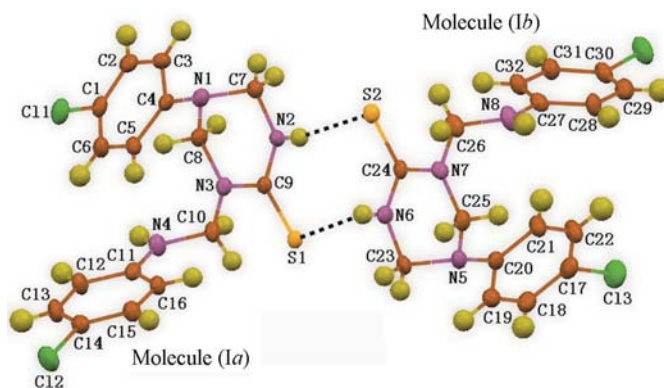


**Figure 1**
The two independent molecules in compound (I). Displacement ellipsoids are drawn at the 16% probability level and H atoms are shown as small spheres of arbitrary radii.
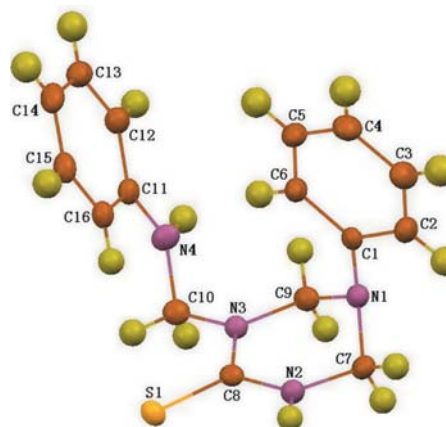


**Figure 2**
The molecular structure of (II), showing the the atom-labelling scheme. Displacement ellipsoids are drawn at the 16% probability level and H atoms are shown as small spheres of arbitrary radii.
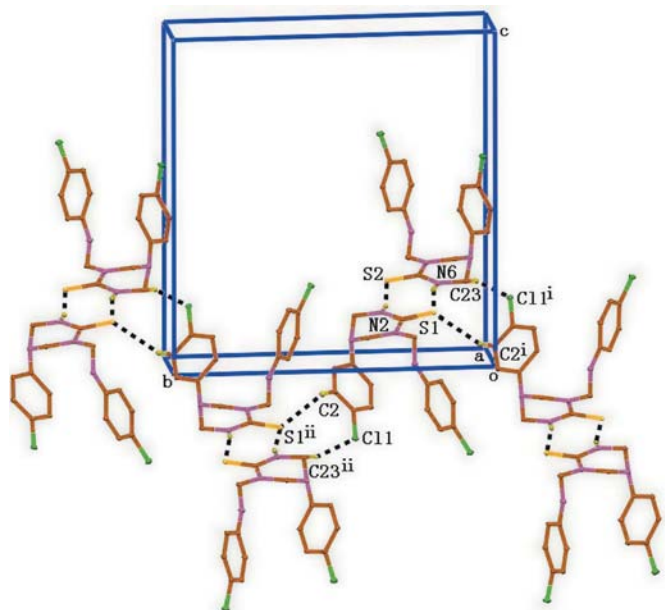
**Figure 3**
Part of the crystal structure of (I), showing the formation of a $C(9)C(14)$ chain parallel to the [010] direction. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Selected atoms are labelled. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $-x$, $-\frac{1}{2} + y$, $-z$; (ii) $-x$, $\frac{1}{2} + y$, $-z$.]

The intramolecular geometries in molecules (I$a$) and (I$b$) present some unexpected features. Within the aryl rings, the C12—C13, C18—C19 and C17—C22 bonds are significantly shorter than those found in similar structural units [1.373 (3)– 1.398 (3) Å; Zhang, Qin *et al.*, 2007], while the C2—C3, C4— C5, C11—C12, C27—C28, C17—C18 and C20—C21 bonds all are longer than the remainder (Table 1). Within the two heterocyclic rings, the N3—C9 and N7—C24 bonds are significantly longer than the N2—C9 and N6—C24 bonds, respectively. In addition, both the N1—C4 and N5—C20 bonds are significantly longer than the N4—C11 and N8—C27 bonds. For the N1—C4 and N5—C20 bonds, these large differences in bond length are probably due to the differences in hybridization state between atoms N1 and N4, N5 and N8, N2 and N3 or N6 and N7. This can be confirmed by the fact that the sums of the interbond angles at atoms N1 and N5 deviate by 20 and 15°, respectively, from 360°, indicating that these two atoms have $sp^3$ character, although they are bonded to the corresponding benzene rings.

Interestingly, all the molecules for (I$a$), (I$b$) and (II) adopt *cis* conformations (Figs. 1 and 2); the phenyl and anilinomethyl groups lie on the same sides of the heterocycle and the dihedral angles between the two aromatic rings in (I$a$), (I$b$) and (II) are 71.13, 67.35 and 71.89°, respectively, indicating that these aromatic rings are nearly perpendicular to one another.

In (II), the heterocycle adopts an envelope conformation; atom N1 is the flap atom, displaced by 0.637 Å from the plane of the other five atoms. The C1—N1 bond is significantly longer than the C11—N4 bond (Table 1). The sum of the three angles around atom N1 is 341.61 (6)° (Table 1), which is significantly smaller than the angle sums around atoms N2, N3
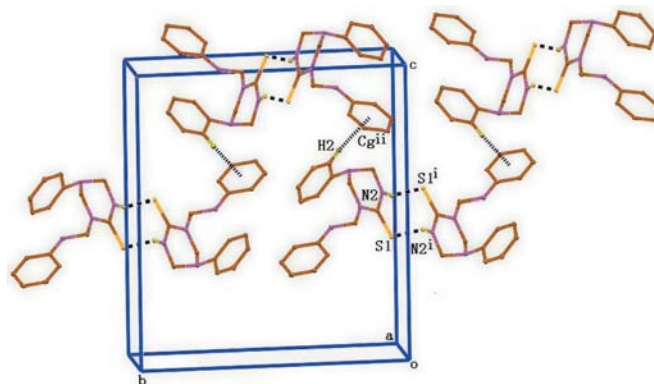


**Figure 4**
Part of the crystal structure of (II), showing the formation of a hydrogen-bonded chain along the $(-\frac{1}{4}, y, \frac{3}{4})$ direction. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Selected atoms are labelled. Dashed lines indicate hydrogen bonds. $Cg$ is the centroid of the C11–C16 ring. [Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.]

or N4. These three features for (II) are similar to the situation in (I).

Within the selected asymmetric unit of (I), the two independent molecules are linked by two weak N—H···S hydrogen bonds (Fig. 1 and Table 2), forming an $R_2^2(8)$ (Bernstein *et al.*, 1995) dimer centred at $(\frac{1}{6}, \frac{1}{4}, \frac{1}{5})$. Dimers of this type are further linked by two weak intermolecular interactions (a C—H···S hydrogen bond and a C—H···Cl contact; Table 2) to form a zigzag chain (Fig. 3). Aromatic ring atom C2 and atom Cl1 in the dimeric unit at $(x, y, z)$ act as hydrogen-bond donors and form intermolecular contacts to, respectively, thiocarbonyl atom S1 and atom H23$A$ in the molecule at $(-x, y + \frac{1}{2}, -z)$ (Table 2), so generating by inversion a $C(9)C(14)$ chain of $R_2^2(8)$ rings along the [010] direction (Fig. 3). Two such chains pass through each unit cell; they are related to one another by propagation and hence are parallel. There are no direction-specific interactions between the two chains.

In compound (II) (Fig. 2 and Table 3), the molecules are linked into sheets of considerable complexity by two hydrogen bonds, one of N—H···S type and one of C—H···$\pi$(arene) type (Table 4). However, the two-dimensional structure is readily analysed in terms of two relatively simple one-dimensional substructures. In the first substructure, atom N2 in the molecule at $(x, y, z)$ acts as a hydrogen-bond donor to atom S1 in the molecule at $(-x, -y, -z + 1)$, so generating by inversion a dimer centred at $(0, 0, \frac{1}{2})$ and characterized by the usual $R_2^2(8)$ motif (Fig. 4). The dimer can be regarded as the backbone building unit, from which the first substructure is built by only one C—H···$\pi$ hydrogen bond. Atom C2 in the molecule at $(x, y, z)$, part of the dimer at $(0, 0, \frac{1}{2})$, acts as hydrogen-bond donor to the C11–C16 ring in the molecule at $(-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, which is part of the dimer centred at $(-\frac{1}{2}, \frac{1}{2}, 1)$. Propagation by inversion then generates a $C_2^2(8)$ chain along $(-\frac{1}{4}, y, \frac{3}{4})$ (Fig. 4). In the second substructure, atom C2 in the molecule at $(x, y, z)$ acts as hydrogen-bond donor to the C11–C16 ring in the molecule at $(x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2})$, so forming a hydrogen-bonded chain running along the [$\bar{1}01$] direction and generated by a $2_1$ screw axis along [$\bar{1}01$] (Fig. 5).
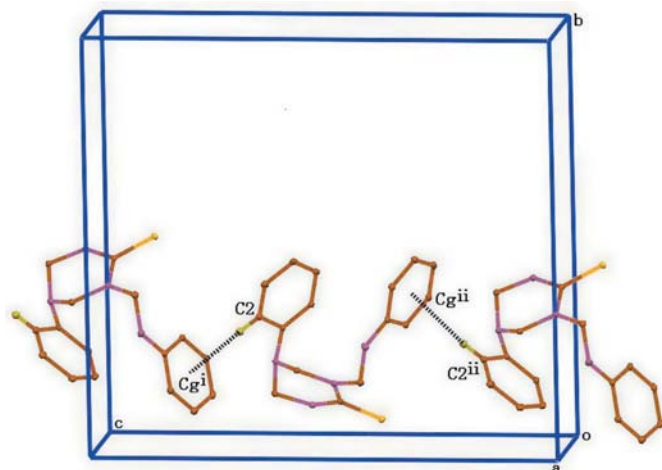
**Figure 5**
Part of the crystal structure of (II), showing the formation of a hydrogen-bonded chain running along the [$\bar{1}$01] direction. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Selected atoms are labelled. Dashed lines indicate hydrogen bonds. $Cg$ is the centroid of the C11–C16 ring. [Symmetry codes: (i) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$.]

The combination of these two chain motifs is sufficient to link all the molecules into a two-demensional sheet parallel to [101]. Two such sheets pass through each unit cell, in the domains $0 < x < 1$, $0 < z < 1$ and $1 < x < 2$, $1 < z < 2$, and there are no direction-specific interactions between the two sheets.

## Experimental

Brief details of the syntheses of the title compounds, (I) and (II), will be reported elsewhere (Zhang *et al.*, 2008). Crystals of (I) were obtained by recrystallization from dimethyl sulfoxide. $^1$H NMR (DMSO, 400 MHz): $\delta$ 8.37 (*s*, 1H), 6.796–7.076 (*m*, 8H), 6.59 (*t*, *J* = 6.8 Hz, 1H), 5.20–5.19 (*d*, *J* = 6.8 Hz, 2H), 4.78 (*s*, 2H), 4.57 (*s*, 2H). Crystals of (II) were obtained by recrystallization from acetonitrile. $^1$H NMR (DMSO, 400 MHz): $\delta$ 8.30 (*s*, 1H), 7.10–6.58 (*m*, 10H), 6.45 (*t*, *J* = 7.2 Hz, 1H), 5.23 (*d*, *J* = 6.8 Hz, 2H), 4.79 (*s*, 2H), 4.57 (*s*, 2H).

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

| | | | |
|---|---|---|---|
| N1—C8 | 1.437 (7) | C15—C16 | 1.379 (8) |
| N1—C4 | 1.438 (7) | N5—C20 | 1.437 (7) |
| N1—C7 | 1.468 (7) | N6—C24 | 1.331 (6) |
| N2—C9 | 1.354 (6) | N7—C24 | 1.362 (6) |
| N3—C9 | 1.386 (6) | N8—C27 | 1.382 (7) |
| N4—C11 | 1.385 (7) | C17—C22 | 1.340 (9) |
| C1—C2 | 1.365 (8) | C17—C18 | 1.406 (10) |
| C1—C6 | 1.383 (8) | C18—C19 | 1.357 (8) |
| C2—C3 | 1.401 (8) | C19—C20 | 1.394 (8) |
| C3—C4 | 1.385 (8) | C20—C21 | 1.403 (8) |
| C4—C5 | 1.418 (8) | C21—C22 | 1.380 (9) |
| C5—C6 | 1.384 (8) | C27—C32 | 1.395 (8) |
| C11—C16 | 1.388 (7) | C27—C28 | 1.412 (8) |
| C11—C12 | 1.415 (8) | C28—C29 | 1.366 (8) |
| C12—C13 | 1.358 (9) | C29—C30 | 1.382 (9) |
| C13—C14 | 1.391 (9) | C30—C31 | 1.381 (9) |
| C14—C15 | 1.377 (8) | | |
| | | | |
| C8—N1—C4 | 118.1 (5) | C25—N5—C20 | 120.2 (5) |
| C8—N1—C7 | 108.2 (4) | C25—N5—C23 | 107.8 (5) |
| C4—N1—C7 | 114.2 (4) | C20—N5—C23 | 116.7 (5) |

**Table 2**
Hydrogen-bond geometry (Å, °) for (I).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N6—H6$D\cdots$S1 | 0.86 | 2.52 | 3.356 (4) | 164 |
| N2—H2$D\cdots$S2 | 0.86 | 2.59 | 3.430 (4) | 167 |
| C2—H2$\cdots$S1$^i$ | 0.93 | 2.93 | 3.743 (4) | 147 |
| C23—H23$A\cdots$Cl1$^{ii}$ | 0.97 | 2.86 | 3.783 (7) | 160 |

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

## Compound (I)

### Crystal data

| | |
|---|---|
| $C_{16}H_{16}Cl_2N_4S$ | $V = 1717.3$ (9) Å$^3$ |
| $M_r = 367.29$ | $Z = 4$ |
| Monoclinic, $P2_1$ | Mo $K\alpha$ radiation |
| $a = 5.9271$ (17) Å | $\mu = 0.50$ mm$^{-1}$ |
| $b = 16.398$ (5) Å | $T = 291$ (2) K |
| $c = 17.864$ (5) Å | $0.38 \times 0.30 \times 0.24$ mm |
| $\beta = 98.468$ (4)° | |

### Data collection

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 13046 measured reflections |
| | 6252 independent reflections |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | 3942 reflections with $I > 2\sigma(I)$ |
| $T_{min} = 0.832$, $T_{max} = 0.889$ | $R_{int} = 0.044$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.061$ | H-atom parameters constrained |
| $wR(F^2) = 0.165$ | $\Delta\rho_{max} = 0.43$ e Å$^{-3}$ |
| $S = 1.01$ | $\Delta\rho_{min} = -0.27$ e Å$^{-3}$ |
| 6252 reflections | Absolute structure: Flack (1983), with 685 Friedel pairs |
| 415 parameters | Flack parameter: 0.00 (2) |
| 1 restraint | |

## Compound (II)

### Crystal data

| | |
|---|---|
| $C_{16}H_{18}N_4S$ | $\gamma = 90.00°$ |
| $M_r = 298.40$ | $V = 1565.9$ (4) Å$^3$ |
| Mmnoclinic, $P2_1/n$ | $Z = 4$ |
| $a = 5.8564$ (8) Å | Mo $K\alpha$ radiation |
| $b = 15.486$ (2) Å | $\mu = 0.21$ mm$^{-1}$ |
| $c = 17.285$ (2) Å | $T = 291$ (2) K |
| $\alpha = 90.00°$ | $0.35 \times 0.27 \times 0.21$ mm |
| $\beta = 92.660$ (2)° | |

### Data collection

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 11424 measured reflections |
| | 2895 independent reflections |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | 2151 reflections with $I > 2\sigma(I)$ |
| $T_{min} = 0.931$, $T_{max} = 0.957$ | $R_{int} = 0.026$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | 190 parameters |
| $wR(F^2) = 0.094$ | H-atom parameters constrained |
| $S = 1.03$ | $\Delta\rho_{max} = 0.15$ e Å$^{-3}$ |
| 2895 reflections | $\Delta\rho_{min} = -0.13$ e Å$^{-3}$ |

H atoms were placed in idealized positions and allowed to ride on their respective parent atoms, with C—H = 0.98 Å and N—H = 0.86 Å, and with $U_{iso}$(H) = $1.2U_{eq}$(C,N).

# organic compounds

## Table 3
Selected geometric parameters (Å, °) for (II).

| | | | |
|---|---|---|---|
| N1—C1 | 1.424 (2) | N3—C8 | 1.348 (2) |
| N2—C8 | 1.339 (2) | N4—C11 | 1.391 (2) |
| | | | |
| C1—N1—C9 | 117.8 (2) | C8—N3—C10 | 123.1 (2) |
| C1—N1—C7 | 115.7 (2) | C8—N3—C9 | 120.6 (2) |
| C9—N1—C7 | 108.1 (2) | C10—N3—C9 | 114.9 (1) |

## Table 4
Hydrogen-bond geometry (Å, °) for (II).

$Cg$ is the centroid of the C11–C16 ring.

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N2—H2$D\cdots$S1$^i$ | 0.86 | 2.57 | 3.394 (2) | 160 |
| C2—H2$\cdots Cg^{ii}$ | 0.93 | 2.87 | 3.765 (2) | 163 |

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

For both compounds, data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3065). Services for accessing these data are described at the back of the journal.

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