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4-Amino-6-phenyl-3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-one

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.003 Å
R factor = 0.049
wR factor = 0.143
Data-to-parameter ratio = 18.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound $C_9H_8N_4OS$, crystallizes with two molecules in the asymmetric unit. The crystal structure is stabilized by intermolecular hydrogen bonds between the protonated N atom of the triazine ring and the carbonyl O atom of an adjacent triazine ring, forming chains running parallel to the *a* axis.

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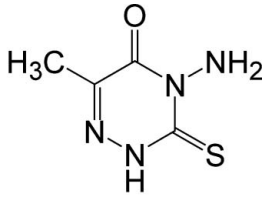
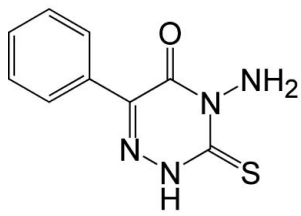
Comment

1,2,4-Triazines and many compounds derived from them are found to possess a wide variety of pharmacological and herbicidal activities (Holla *et al.*, 1999; Gruzdyev *et al.*, 1983; Abdel-Rahman, 2001; Sathiakumar & Delzell, 1997). In addition to its biological activity, there has been considerable interest in the chemistry of 4-amino-6-methyl-3-thioxo-3,4-dihydro-2H-1,2,4-triazin-5-one, (I), known in biochemical research as 6-azathiothymine or 6-ATT. Not only has its structure been determined (Voutsas, *et al.*, 1978; Ghassemzadeh, *et al.*, 1998), but the structures of its complexes with copper (Razak, *et al.*, 1999; Ghassemzadeh, *et al.*, 2002; Ghassemzadeh, *et al.*, 2004; Yazdanbakhsh, *et al.*, 2004), silver (Adhami, *et al.*, 1999; Ghassemzadeh, *et al.*, 2004), palladium (Neumuller, *et al.*, 1999; Ghassemzadeh, *et al.*, 1998; Ghassemzadeh, *et al.*, 2000; Ghassemzadeh, *et al.*, 2005), platinum (Ghassemzadeh, *et al.*, 2005), and lithium (Ghassemzadeh, *et al.*, 2003) have been reported. The structure of a related derivative, 4-amino-6-*tert*-butyl-3-thioxo-3,4-dihydro-2H-1,2,4-triazin-5-one has also been recently reported (Sridhar *et al.*, 2006).



(I)



(II)

In view of this interest in (I) and its derivatives, the crystal structure of 4-amino-6-phenyl-3-thioxo-3,4-dihydro-2H-1,2,4-

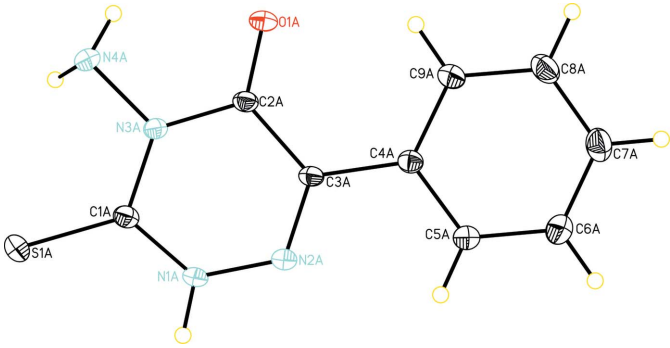


Figure 1
View of one of the two essentially identical molecules of (II) in the asymmetric unit, showing its atom-numbering scheme; the molecule not shown is numbered identically, except its labels bear the suffix B. Displacement ellipsoids are drawn at the 50% probability level.

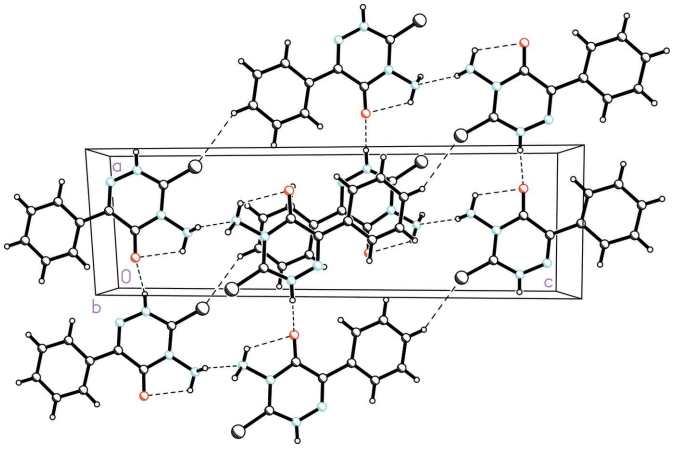


Figure 2
The molecular packing for (II), viewed down the *b* axis, showing the chains formed along the *a* axis. The vertical chain in the center of this view contains only A-type molecules, while the chains at each end of the cell contain B-type molecules. Dashed lines indicated hydrogen bonds.

triazin-5-one (II), is reported here. It crystallizes in the triclinic space group $P\overline{1}$ with two molecules in the asymmetric unit. In all essential details, the molecular geometries of both molecules (Fig. 1 and Table 1) are identical and are in good agreement with related structures containing the 5-oxo-3-thioxo-1,2,4-triazine system (Ghassemzadeh *et al.*, 1998; Sridhar *et al.*, 2006). The triazine ring is planar and exists in the thione form; the C═S bond lengths are slightly longer than that expected for a pure double bond (1.61 Å; Pauling, 1960). The N—N bond distances are intermediate between those expected for single (1.45 Å) and double (1.20 Å) bonds. The C—N bonds show marked differences in their lengths, those between N2 and C3 being the shortest and those between N3 and C2 being the longest. These values are intermediate between those expected for single and double C—N bonds (1.47 and 1.27 Å, respectively).

The crystal structure is stabilized by intermolecular N—H···O hydrogen bonds (Table 2). The two molecules of the asymmetric unit display similar, but not identical, packing interactions. In each case, the protonated N atom (N1*A* or N1*B*) of the triazine ring links to the carbonyl O atom of an adjacent molecule of the same type, forming a chain running parallel to the *a* axis (Figs. 2 and 3).

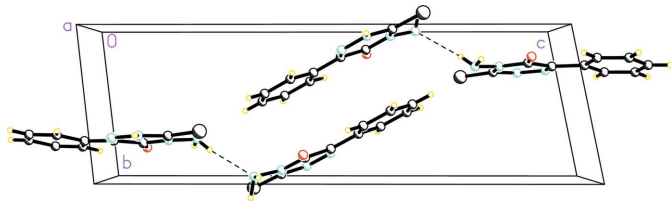


Figure 3
The molecular packing for (II), viewed down the *a* axis, showing the hydrogen bonds (dashed lines) linking chains of A-type molecules and B-type molecules.

Experimental

Benzoylformic acid (15g, 0.1mol) was mixed with thiocarbohydrazide (10.6g, 0.1 mol) in 500 ml water and the mixture was heated to boiling (Dornow *et al.*, 1964). A yellow precipitate separated and was filtered. The product was recrystallized from an acetone–toluene (1:1) mixture (yield: 91.8%; m.p. 506 K). Elemental analysis (calculated) (%): C 49.22 (49.09); H 3.53 (3.64); N 25.65 (25.45).

Crystal data

$C_9H_8N_4OS$
M_r = 220.25
Triclinic, $P\overline{1}$
a = 6.5965 (11) Å
b = 7.0573 (12) Å
c = 21.238 (4) Å
α = 81.061 (3)°
β = 89.307 (4)°
γ = 75.444 (3)°
V = 945.0 (3) Å^3
Z = 4
D_x = 1.548 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 273 (2) K
Plate, colourless
0.55 × 0.27 × 0.10 mm

Data collection

Bruker Apex II CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.845, T_{max} = 0.970
10897 measured reflections
5336 independent reflections
3757 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 30.8°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.143
S = 1.05
5336 reflections
289 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.071P)^2 + 0.1411P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Selected bond lengths (Å).

S1*A*—C1*A*	1.6541 (17)	N3*A*—C1*A*	1.371 (2)
S1*B*—C1*B*	1.6520 (18)	N3*A*—C2*A*	1.385 (2)
O1*A*—C2*A*	1.223 (2)	N1*B*—N2*B*	1.341 (2)
O1*B*—C2*B*	1.220 (2)	N1*B*—C1*B*	1.352 (2)
N1*A*—N2*A*	1.342 (2)	N2*B*—C3*B*	1.298 (2)
N1*A*—C1*A*	1.353 (2)	N3*B*—C1*B*	1.367 (2)
N2*A*—C3*A*	1.298 (2)	N3*B*—C2*B*	1.391 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1AA···O1A^{i}	0.88 (2)	2.00 (2)	2.810 (2)	153 (2)
N4A—H4$A2$···O1A	0.81 (3)	2.22 (2)	2.643 (2)	112 (2)
N1B—H1BA···O1B^{i}	0.82 (2)	2.02 (2)	2.806 (2)	158 (2)
N4B—H4$B1$···N4A^{ii}	0.84 (3)	2.41 (3)	3.228 (3)	167 (2)
N4B—H4$B2$···O1B	0.86 (3)	2.20 (2)	2.633 (2)	111.3 (19)

Symmetry codes: (i) $x+1, y, z$; (ii) $-x, -y+1, -z+1$.

All C-bound H atoms were initially located in a difference Fourier map, and were then placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances in the range 0.95–1.00 Å, and U_{iso}(H) = 1.2U_{eq}(C). Positional parameters for N-bound H atoms were refined and U_{iso}(H) = 1.2U_{eq}(N).

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2* (Bruker, 2006); data reduction: *APEX2* (Bruker, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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