

Thionordazepam: strong intermolecular N—H···N hydrogen-bonded chains

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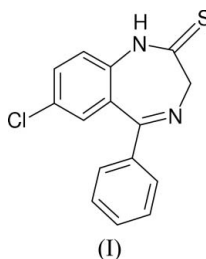
Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
 R factor = 0.062
 wR factor = 0.142
Data-to-parameter ratio = 17.3

In the title compound, 7-chloro-1,3-dihydro-5-phenyl-2*H*-1,4-benzodiazepine-2-thione, $\text{C}_{15}\text{H}_{11}\text{ClN}_2\text{S}$, the central seven-membered diazepinethione ring adopts a boat conformation. The dihedral angle between the planes of the aromatic rings is $63.7(1)^\circ$. The crystal packing is determined by strong N—H···N hydrogen bonds, generating a one-dimensional chain along [001].

Comment

Benzodiazepines represent a very important class of compounds, collectively referred to as anxiolytics, which act as indirect agonists by binding to the GABA-A receptor, a primary inhibitory neurotransmitter in the central nervous system (Williams *et al.*, 2002). The title compound, 7-chloro-1,3-dihydro-5-phenyl-2*H*-1,4-benzodiazepine-2-thione, (I), commercially known as thionordazepam, is one of the derivatives of benzodiazepine, which is used for the preparation of anxiolytic alprazolam (Wang & De Vane, 2003).



The structure of (I) is illustrated in Fig. 1. In (I), the planes defined by aromatic rings C1–C6 and C10–C15 form a dihedral angle of $63.7(1)^\circ$. The central seven-membered diazepinethione ring (atoms C4/C5/C7–C9/N1/N2) adopts a boat conformation. The boat conformation is predominantly observed for the seven-membered ring of benzodiazepine and its derivatives, even with different double-bond positions and widely differing substituents (Walkinshaw, 1985; Torres *et al.*, 2005). The internal torsion angles of the ring are shown in Fig. 1. The Cremer and Pople puckering parameters (Cremer & Pople, 1975) are $q_2 = 0.817(5)$ Å, $q_3 = 0.245(5)$ Å, $\varphi_2 = 26.5(3)^\circ$ and $\varphi_3 = 130(1)^\circ$; and the total puckering amplitude $Q_T = 0.853(5)$ Å. The asymmetry parameter, measured as the root-mean-square of the sum of the torsion angles, related by a mirror plane (Duax *et al.*, 1976), passing through atom C8 and bisecting the C4–C5 bond, is marginal, *i.e.* $\Delta C_s = 3.2(5)^\circ$, indicating a near ideal boat conformation of the ring. The overall molecular conformation is additionally described by the rotation about the C9–C10 bond; the torsion angle C5–C9–C10–C15 is $39.1(6)^\circ$.

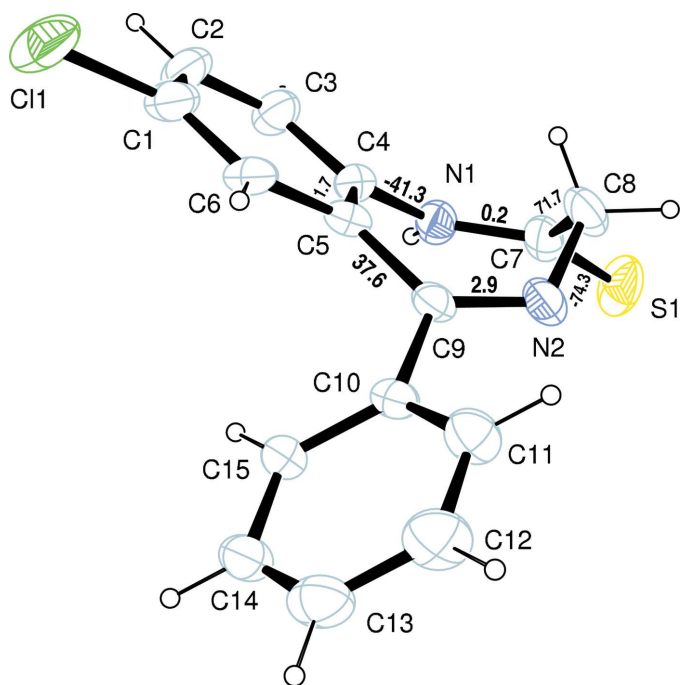


Figure 1
A view of (I), showing 20% probability displacement ellipsoids and the atom-numbering scheme. The numerical figures refer to the internal torsion angles ($^{\circ}$) of the central diazepinethione ring in a boat conformation (s.u. values lie in the range 0.5–0.6 $^{\circ}$). H atoms are shown as small spheres of arbitrary radii.

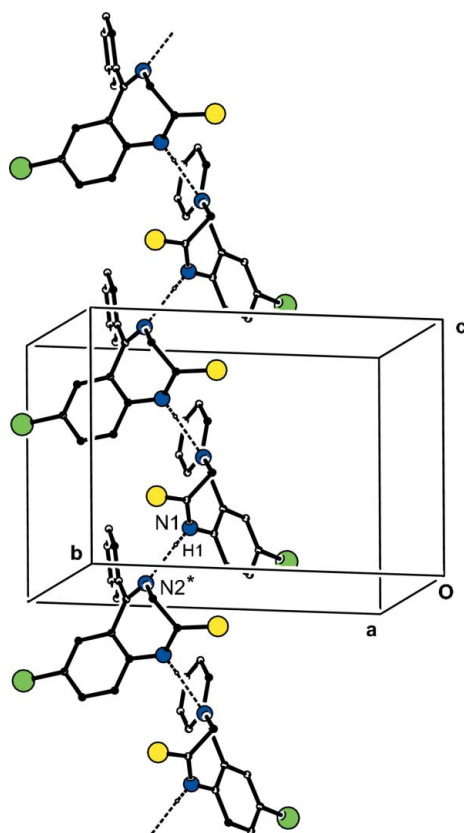


Figure 2
Part of the crystal packing of (I), showing N–H \cdots N hydrogen-bonded (dashed lines) chains along [001]. The atom labelled with an asterisk (*) is at the symmetry position $(x, \frac{3}{2} - y, z - \frac{1}{2})$. Color key: C black, N blue, S yellow and Cl green.

The molecules in the crystal structure are linked by strong intermolecular N–H \cdots N hydrogen bonds (Table 1). Strong N–H \cdots N bonds, presumably low-barrier hydrogen bonds, have been generally observed as intramolecular (Hilbert & Emsley, 1990; Perrin & Nielson, 1997). The N–H \cdots N hydrogen bonds link symmetry-related molecules into a chain along [001], as shown in Fig. 2. In contrast to the similar structures of halogen derivatives of benzodiazepine reported previously (Prasanna & Guru Row, 2000), the molecular assembly in the present case does not display any direction-specific halogen or aromatic interactions.

Experimental

The title compound was obtained from Lake Chemicals, Bangalore. Single crystals suitable for X-ray diffraction were grown by slow evaporation of an ethyl acetate solution.

Crystal data

C₁₅H₁₁ClN₂S
M_r = 286.77
 Orthorhombic, *Pnc2*
a = 9.993 (2) Å
b = 14.223 (3) Å
c = 10.175 (2) Å
V = 1446.2 (5) Å³
Z = 4
D_x = 1.317 Mg m^{−3}

Mo *K*α radiation
 Cell parameters from 1456 reflections
 θ = 5–35 $^{\circ}$
 μ = 0.40 mm^{−1}
T = 293 (2) K
 Thin plate, colourless
 0.5 × 0.3 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.865, *T_{max}* = 0.972
 10960 measured reflections

3021 independent reflections
 1505 reflections with *I* > 2 σ (*I*)
R_{int} = 0.057
 θ_{\max} = 27.4 $^{\circ}$
h = −11 → 12
k = −18 → 17
l = −13 → 13

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.062
wR (*F*²) = 0.142
S = 1.00
 3021 reflections
 175 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.25 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.15 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 1358 Friedel pairs
 Flack parameter: 0.42 (11)

Table 1

Hydrogen-bond geometry (Å, $^{\circ}$).

D–H \cdots A	D–H	H \cdots A	D \cdots A	D–H \cdots A
N1–H1 \cdots N2 ⁱ	0.88 (1)	1.95 (3)	2.827 (5)	177 (3)

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

Atom H1 was located in a difference Fourier map and was refined with an N–H distance restraint of 0.88 (1) Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. All other H atoms were positioned geometrically and refined as riding on their carrier atoms, with aromatic C–H = 0.93 Å, methylene C–H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The authenticity of the high value of Flack (1983) parameter [0.4 (1)] was evaluated by refining inversion twin contributions. This yielded the same, 0.4 (1) value of the batch scale factor, indicating that the structure could be a

mixture of inversion twin components having contributions of 0.4 and 0.6. Since treatment of the inversion twin in this way did not significantly improve the *R* values and other indicators of the refinement, the present structure is reported without such treatment.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PARST* (Nardelli, 1995).

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