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

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.062
wR factor = 0.142
Data-to-parameter ratio = 17.3

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

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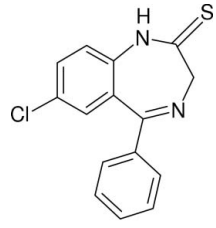
In the title compound, 7-chloro-1,3-dihydro-5-phenyl-2*H*-1,4-benzodiazepine-2-thione, $C_{15}H_{11}ClN_2S$, the central seven-membered diazepinethione ring adopts a boat conformation. The dihedral angle between the planes of the aromatic rings is 63.7 (1)°. The crystal packing is determined by strong 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).



(I)

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)°. The central seven-membered diazepinthione 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, φ_2 = 26.5 (3)° and φ_3 = 130 (1)°; 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.* ΔC_s = 3.2 (5)°, 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)°.

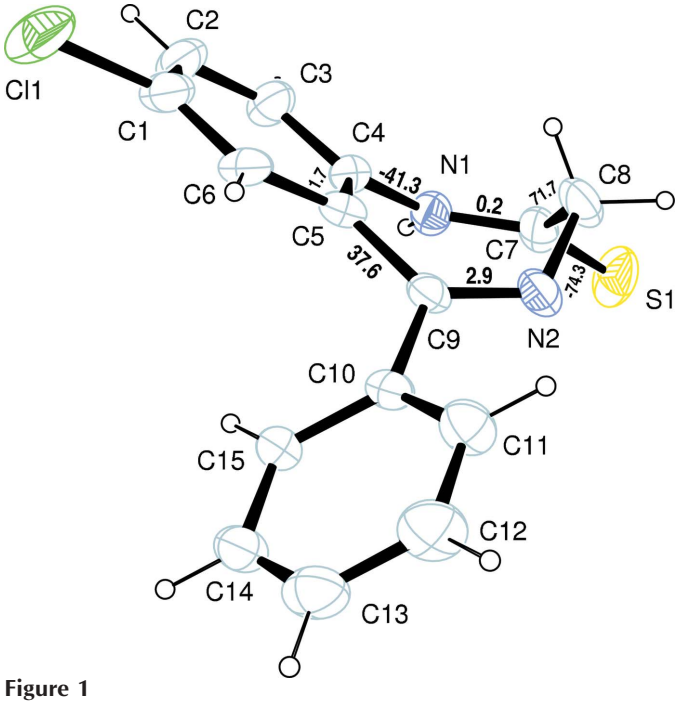


Figure 1
A view of (I), showing 20% probability displacement ellipsoids and the atom-numbering scheme. The numerical figures refer to the internal torsion angles (°) of the central diazepinethione ring in a boat conformation (s.u. values lie in the range 0.5–0.6°). H atoms are shown as small spheres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

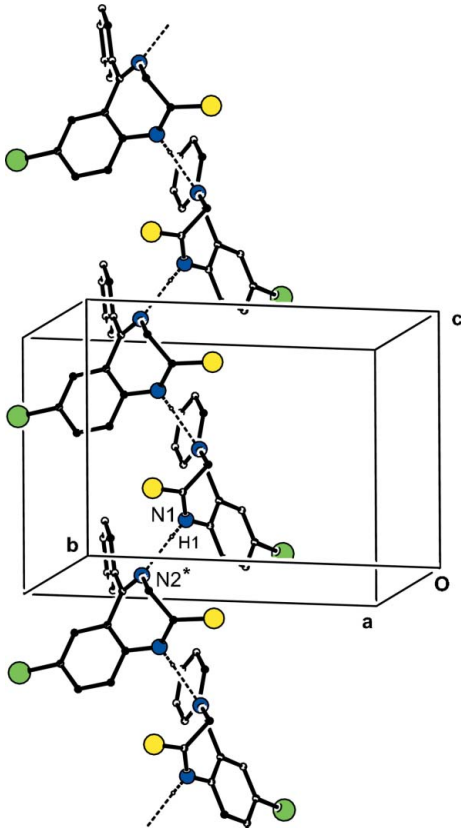


Figure 2
Part of the crystal packing of (I), showing N—H···N hydrogen-bonded (dashed lines) chains along [001]. The atom labelled with an asterisk (*) is at the symmetry position ($x, \frac{3}{2}-y, z-\frac{1}{2}$). Color key: C black, N blue, S yellow and Cl green.

The molecules in the crystal structure are linked by strong intermolecular N—H···N hydrogen bonds (Table 1). Strong N—H···N bonds, presumably low-barrier hydrogen bonds, have been generally observed as intramolecular (Hilbert & Emsley, 1990; Perrin & Nielson, 1997). The N—H···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

$C_{15}H_{11}ClN_2S$
$M_r = 286.77$
Orthorhombic, *Pnc*2
$a = 9.993$ (2) Å
$b = 14.223$ (3) Å
$c = 10.175$ (2) Å
$V = 1446.2$ (5) Å^3
$Z = 4$
$D_x = 1.317$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1456 reflections
$\theta = 5$–35°
$\mu = 0.40$ 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 $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 27.4°$
$h = -11 \rightarrow 12$
$k = -18 \rightarrow 17$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.142$
$S = 1.00$
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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}
Absolute structure: Flack (1983), 1358 Friedel pairs
Flack parameter: 0.42 (11)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···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_{iso}(H) = 1.2U_{eq}(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_{iso}(H) = 1.2U_{eq}(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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