Crystal Structure of Bis(3,4-dihydroisoquinolin-2(1*H*)-yl)methanethione

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The title compound, bis(3,4-dihydroisoquinolin-2(1*H*)-yl)methanethione (C₁₉H₂₀N₂S), crystallizes in the orthorhombic space group *Pbcn* with the following unit-cell parameters: *a* = 4.8145(3), *b* = 12.6749(9), *c* = 26.292(2) Å, *Z* = 4. The final reliability factor is *R* = 0.0366 for 1441 observed reflections, and the goodness of the fit is equal to 1.015. The molecule lies on a crystallographic twofold axis that is coincident with the C=S bond. The N-containing six-membered ring adopts a *half-chair* conformation. The crystal structure consists of a polymeric arrangement of molecules linked through C-H...S interactions.

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Thiones, also known as thioketones, are organosulfur compounds related to conventional ketones. Thiones have a wide range of applications: as analytical reagents, as metal corrosion inhibitors, and potent inhibitors of tyrosinase.^{1,2} Metal complexes of thiones exhibit interesting anticarcinogenic properties,³ including enzyme inhibition,⁴ and are used in the treatment of rheumatoid arthritis.⁵ Thermal decomposition and the oxidation of dithiocarbamates yielded various products, such as isothiocyanates, disulfides and thiones.⁶ In this case, bis(3,4-dihydroisoquinolin-2(1*H*)-yl)methanethione is obtained by a simple decomposition of Na(thiqdte)·2H₂O (where thiqdte = 1,2,3,4-tetrahydroisoquinolinecarbodithioate anion); single crystals were grown from the mixture of a toluene and ethanol solution. The investigated compound (Fig. 1), m.p. 86°C, was characterized by spectral data. To further confirm the structure, and to study the role of various intermolecular interactions, a comprehensive X-ray analysis of the molecule is reported.

¹H NMR (CDCl₃): δ = 3.09 (t, H-4), 3.80 (t, H-3), 4.77 (s, H-1), 7.12 – 7.24 ppm (m, aromatic protons).

¹³C NMR (CDCl₃): δ = 28.7 (C-4), 49.5 (C-3), 53.5 (C-1), 126.3 – 134.5 (aromatic carbons), 193.6 ppm (C=S).

A yellow block-shaped single crystal of the title compound, measuring 0.25 × 0.20 × 0.20 mm, was picked up for X-ray intensity data collection on a Bruker CCD area-detector diffractometer equipped with graphite monochromated Mo *K*_α radiation (λ = 0.71073 Å). A total of 9449 reflections were collected, of which 1441 reflections were treated as observed (*I*

> 2σ(*I*)). Data were corrected for Lorentz, polarization and absorption factors.

The structure was solved by direct methods using SHELXS97, and refined by SHELXL97.⁷ All hydrogen atoms were located from a difference electron density map, and their positional and isotropic thermal parameters were included in the refinement. The final refinement cycle yielded an *R*-factor of 0.0366 [*wR* (*F*²) = 0.1242]. The residual electron density ranged from –0.165 to 0.290 eÅ^{–3}. The CIF for this structure has been deposited at Cambridge Crystal Data Centre (CCDC 827224). The crystallographic data are summarized in Table 1. Selected

Table 1 Crystal and experimental data

Chemical formula: C ₁₉ H ₂₀ N ₂ S	
Formula weight = 308.43	
<i>T</i> = 293(2) K	
Crystal system: orthorhombic	Space group: <i>Pbcn</i>
<i>a</i> = 4.8145(3) Å	
<i>b</i> = 12.6749(9) Å	
<i>c</i> = 26.2919(19) Å	
<i>V</i> = 1604.42(19) Å ³	<i>Z</i> = 4
<i>D</i> _x = 1.277 g/cm ³	<i>D</i> _m (floatation) = not measured
Radiation: Mo <i>K</i> _α (λ = 0.71073 Å)	
μ(Mo <i>K</i> _α) = 0.200 mm ^{–1}	<i>F</i> (0 0 0) = 656
Crystal size = 0.25 × 0.20 × 0.20 mm ³	
No. of reflections collected = 9449	
No. of independent reflections = 1756	
θ range for data collection: 3.10 to 26.99°	
Data/Restraints/Parameters = 1756/0/141	
Goodness-of-fit on <i>F</i> ² = 1.015	
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]: <i>R</i> 1 = 0.0366, <i>wR</i> 2 = 0.1164	
<i>R</i> indices (all data): <i>R</i> 1 = 0.0460, <i>wR</i> 2 = 0.1242	
(Δρ) _{max} = –0.001	
(Δρ) _{max} = 0.290 eÅ ^{–3}	(Δρ) _{min} = –0.165 eÅ ^{–3}
Measurement: Bruker CCD area-detector diffractometer	
Programs system: SHELXL-97, SADABS	
Structure determination: SHELXS-97	
CCDC deposition number: 827224

Fig. 1 Chemical diagram of the title compound.

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Table 2 Selected bond lengths (Å), bond angles (°) and torsion angles (°) for non hydrogen atoms (e.s.d.'s are given in parentheses)

Bond Lengths			
S1 - C11	1.691(2)	C1 - N2	1.465(2)
C1 - C9	1.506(2)	N2 - C11	1.351(1)
N2 - C3	1.462(2)	C3 - C4	1.514(2)
C4 - C10	1.504(2)	C11 - N2	1.3513(1)
Bond Angles			
N2 - C1 - C9	112(1)	C11 - N2 - C3	122.1(1)
C11 - N2 - C1	122.9(1)	C3 - N2 - C1	112.6(1)
N2 - C3 - C4	111.1(1)	N2 - C11 - N2	117(2)
N2 - C11 - S1	121.52(8)	N2 - C11 - S1	121.52(8)
Torsion Angles			
C9 - C1 - N2 - C3	45.7(1)	C1 - N2 - C3 - C4	-64.2(2)
N2 - C3 - C4 - C10	47.2(2)	N2 - C1 - C9 - C10	-13.9(2)
C1 - C9 - C10 - C4	-0.2(2)	C3 - C4 - C10 - C9	-16.3(2)

Fig. 2 ORTEP view of the molecule, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

bond lengths, bond angles and torsion angles are given in Table 2.

An ORTEP view of the title molecule is shown in Fig. 2. The molecule lies on a crystallographic two-fold axis that passes through the C11 and S1 atoms. The C11-S1 bond length in the title compound, *i.e.*, [1.691(2)Å], is comparable to the C=S distance in, for example 5-(4-methoxyphenyl)-4-methylthiazole-2(3*H*)thione [1.679(3)Å]⁸ and quinolin-2(1*H*)-thione [1.686(2) Å].⁹ The C11-N2 bond distance [1.351(1)Å] is intermediate between standard single C-N (1.47 Å) and double C=N (1.28 Å) bonds, being significantly shorter than the C1-N2 [1.465(2)Å] and C3-N2 [1.462(2)Å] bonds, because atom C11 is in an sp²-hybridized state, while atoms C1 and C3 are sp³-hybridized. The coplanarity of the N2/C11/S1/N2' fragment is similar to the situation found in other thiones.¹⁰ Ring A is in a *half-chair* conformation. The phenyl ring B is perfectly planar. The dihedral angle between the heterocyclic ring A and phenyl ring

Table 3 Geometry of hydrogen bonds

D-H...A	D-H(Å)	H...A(Å)	D...A(Å)	∠[D-H...A(°)]
C1-H1A...S1 ⁱ	0.98(2)	2.83(2)	3.764(2)	159(1)

Symmetry Code (i) $-x+1/2, y-1/2, z$.

Fig. 3 Packing diagram viewed down the *a*-axis.

B is 7.15(5)°.

The packing arrangement of molecules in the unit cell down the *a*-axis is shown in Fig. 3. An intermolecular hydrogen bond, C1-H1A...S1 [H1A...S1 = 2.83(2)Å and C1...S1 = 3.764(2) Å] was observed to form polymeric chains parallel to the *b*-axis.

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