

5-(2-Pyridyl)-1,3-dithiane-2-thione

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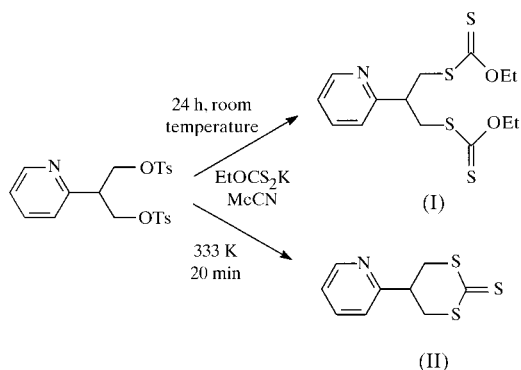
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The title compound, C₉H₉NS₃, crystallizes with two molecules in the asymmetric unit. In both molecules, the dithiane-2-thione rings adopt a symmetric half-boat conformation with the C atom opposite the C—S_{thione} bond out of the plane. The pyridine ring is in an equatorial position and is twisted out of the plane of the half-boat by 82.7 (2) and 84.5 (2)° in the two molecules, so that the N atom is *trans* to the axial C—H bond in both cases.

Comment

We were unsuccessful in reproducing the synthesis of *S,S'*-[2-(2-pyridyl)trimethylene]bis(*O*-ethyl dithiocarbonate), (I) (Uneme *et al.*, 1992). Instead, the previously unknown ring-closed product 5-(2-pyridyl)-1,3-dithiane-2-thione, (II), was recovered. The only important difference in the procedures was that we heated the heterogeneous reaction mixture for a short time.



The crystal structure of (II) has two almost identical molecules in the asymmetric unit (Fig. 1). Both the dithiane-2-thione rings adopt a symmetric half-boat conformation, with the C atom opposite the C—S_{thione} bond out of the plane defined by the other atoms; the largest deviations from the plane are 0.05 (4) Å for S3 and 0.04 (2) Å for S2A. This symmetric half-boat conformation is one of the intermediates postulated for the preferential mode of inversion for the chair form of cyclohexanone (Bucourt & Hainaut, 1967). This conformation is also found for 1,3-dithiane-2-thione in a series

of copper complexes (Bellito *et al.*, 1994). The bond distances (Table 1) found here [S=C 1.658 (1) and 1.662 (1) Å, Csp²—S 1.714 (1)–1.719 (1) Å and S—Csp³ 1.810 (1)–1.815 (1) Å] are very similar to those in the copper complexes, although there the ligand is mono-, di- or tridentate. For both molecules, the pyridine ring is in an equatorial position and is twisted by 82.7 (2) and 84.5 (2)° out of the plane of the half-boat. In both molecules, the N atom is *trans* to the axial C—H bond so that the molecules have approximate mirror symmetry. The two

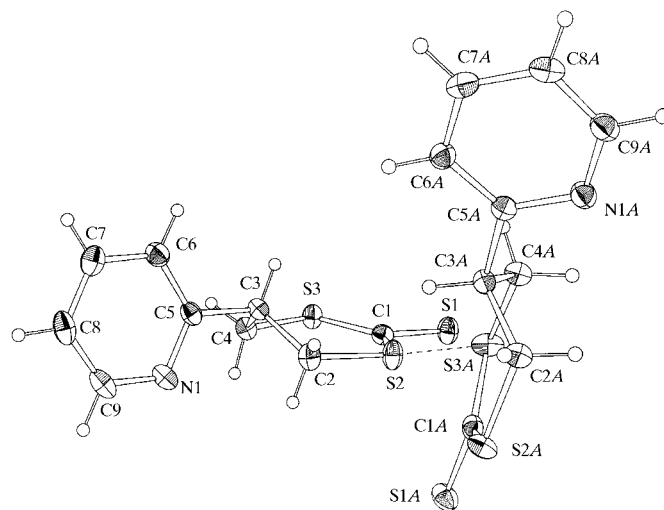


Figure 1

View of the two molecules of the title compound showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii. The short S...S interaction is shown by a dashed line.

molecules are not exactly identical; superimposing the non-H atoms gives a mean-square deviation of 0.42 Å². The difference is mainly in the angle between the C2/C3/C4 and S1/S2/S3/C1/C2/C4 planes, which is 124.8 (2)° for molecule 1 and 120.4 (2)° for molecule 2 (the molecule with suffix A on the labels). This, together with a difference in the angle between C5—C3 and the C2/C3/C4 plane [55.5 (1)° for molecule 1 and 54.0 (1)° for molecule 2] means that the angles between C5—C3 and the S1/S2/S3/C1/C2/C4 plane differ by 6.0 (2)°, so that in molecule 2, the pyridine ring is bent out of plane.

The shortest intermolecular S...S contact is 3.570 (1) Å between S2 and S3A(*x*, − $\frac{1}{2}$ − *y*, $\frac{1}{2}$ + *z*). The *x* and *y* coordinates of the two independent molecules are related approximately by $\frac{3}{2}$ − *x* and −*y*, but there is no simple relation between the *z* coordinates.

Experimental

Triethylamine (3.95 g, 39 mmol) was added dropwise to a solution of 2-(2-pyridyl)-1,3-propanediol (2.40 g, 16 mmol) (Guanti *et al.*, 1997) and *p*-toluenesulfonyl chloride (6.55 g, 34 mmol) in acetonitrile (32 ml) at 273 K over a period of *ca* 30 min. The mixture was kept at 279 K for 24 h and then poured into water (120 ml). An oil precipitated which crystallized after removal of the water and the addition of a little ethanol. The crude product was recrystallized from ethanol, giving 3.10 g (43%) of 2-(pyridyl)trimethylene bis(*p*-toluenesulfonate). ¹H NMR (CDCl₃): δ 2.40 (6H, s), 3.46 (1H, quintet),

4.32 (4H, *d*), 7.0–7.4 (6H, *m*), 7.5–7.8 (5H, *m*), 8.3–8.4 (1H, *m*). ¹³C NMR (CDCl₃): δ 22 (CH₃), 46 (CH), 68 (CH₂), 122.5 (py-C3), 124 (py-C5), 128 (Ar-C3,C5), 130 (Ar-C2,C6), 132 (Ar-C4), 137 (py-C4), 134 (Ar-C1), 149.5 (py-C6), 155.5 (py-C2). A suspension of 2-(pyridyl)trimethylene bis(*p*-toluenesulfonate) (3.1 g, 6.9 mmol) and potassium *O*-ethylthiocarbonate (3.18 g, 20 mmol) in acetonitrile (50 ml) was heated under reflux for 20 min and then poured into water (250 ml). The reaction product was extracted with CHCl₃ (3 × 100 ml) and purified by column chromatography (CH₂Cl₂) to afford a crude product (*ca* 300 mg) and a yellow oil. The crude product was crystallized from ethanol; yield: 200 mg (14%) of (II) as yellow crystals. The crystals used for the structure analysis were deposited from CDCl₃ (m.p. 393–394 K). Analysis calculated for C₉H₉NS₃: C 47.54, H 3.99, N 6.16, S 42.31%; found: C 47.59, H 4.10, N 6.17, S 32.30%. ¹H NMR (CDCl₃): δ 3.2–3.8 (5H, *m*), 7.2–7.4 (3H, *m*), 7.6–7.8 (1H, *m*), 8.5–8.6 (1H, *m*); ¹³C NMR (CDCl₃): δ 39.1 (CH₂), 39.2 (CH), 122.2 (py-C3), 122.7 (py-C5), 137 (py-C4), 150 (py-C6), 160 (py-C2), 220 (C–S); IR: 1010 cm⁻¹, ν(C=S); EIMS: *m/z* 227 (*M*⁺, 58), 194 (23), 180 (17), 162 (11), 150 (10), 136 (26), 118 (32), 106 (100), 79 (25).

Crystal data

C₉H₉NS₃
M_r = 227.38
 Monoclinic, *P*2₁/*c*
a = 17.444 (2) Å
b = 9.6329 (9) Å
c = 12.680 (1) Å
 β = 110.245 (2)°
V = 1999.1 (3) Å³
Z = 8

D_x = 1.511 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 7124 reflections
 θ = 2.5–30.5°
 μ = 0.69 mm⁻¹
T = 120 K
 Plate, yellow
 0.58 × 0.40 × 0.16 mm

Data collection

Siemens SMART CCD diffractometer
 ω rotation scans with narrow frames
 Absorption correction: by integration (*XPREP*; Siemens, 1995)
T_{min} = 0.687, *T_{max}* = 0.894
 25 069 measured reflections
 6191 independent reflections

4802 reflections with *I* > 3σ(*I*)
R_{int} = 0.047
 θ_{max} = 30.5°
h = -24 → 24
k = -13 → 13
l = -17 → 17
 Intensity decay: none

Refinement

Refinement on *F*
R = 0.024
wR = 0.034
S = 1.27
 4802 reflections
 235 parameters

H-atom parameters constrained
w = 1/[σ_{cs}(*F*²) + 1.03*F*²]^{1/2} - |*F*|²
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.48 (5) e Å⁻³
 Δρ_{min} = -0.39 (5) e Å⁻³

Table 1

Selected bond lengths (Å).

S1–C1	1.658 (1)	S1A–C1A	1.662 (1)
S2–C1	1.719 (1)	S2A–C1A	1.717 (1)
S2–C2	1.815 (1)	S2A–C2A	1.810 (1)
S3–C1	1.719 (1)	S3A–C1A	1.714 (1)
S3–C4	1.812 (1)	S3A–C4A	1.815 (1)

The H atoms were included using a riding model and were constrained to have C–H = 0.95 Å and *U*_{iso} = 1.2*U*_{eq} of their parent atom.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1997) and *KRYSTAL* (Hazell, 1995); program(s) used to refine structure: modified *ORFLS* (Busing *et al.*, 1962) and *KRYSTAL*; molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *KRYSTAL*; software used to prepare material for publication: *KRYSTAL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1452). Services for accessing these data are described at the back of the journal.

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