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Azinyl Sulfides. LXVII.[1] 1-Methylpyridine-4(1*H*)-thione

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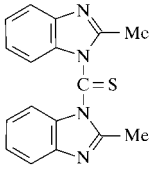
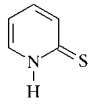
The title compound, C_6H_7NS, is planar, with *endo*-C—N—C bond angles of 118.7 (2) and 118.8 (2)°, and C—S bond lengths of 1.697 (2) and 1.692 (2) Å for the two symmetrically independent molecules. 1-Methylpyridinium-4-thiolate is the major contributor to the molecular structure in the solid state.

Comment

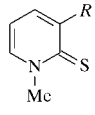
Insight into the nature of the thiocarbonyl group in thiolactams is important, *e.g.* for evaluation of the biological significance of pyrimidinethiones and pyrimidinedithiones as rare bases in RNA or purinethiones (*e.g.* thioguanine) as anticancer drugs (Reynolds, 1989). The synthetic application of thiolactams also seems to depend on their structural features. Due to electronic interactions expressed by mesomerism of the thiocarbonyl group in thioamides, carbon–sulfur bonds in thioamides are a little longer than those in thiones (Rozsondai, 1993) and vary from 1.622 (2) Å in thiocarbonylo-1,1′-bis(2-methylbenzimidazole), (II) (Dolling *et al.*, 1995), to 1.692 (2) or 1.698 (2) Å in 2(1*H*)-pyridinethione, (III) (Ohms *et al.*, 1982), or from 1.677 (3) to 1.691 (4) Å for 3-substituted-1-methyl-2(1*H*)-pyridinethiones, (IV*a,b*) (Dupont *et al.*, 1983, 1984). γ-Azinethiones can be considered as



(II)

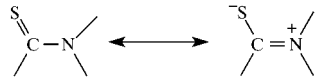


(III)

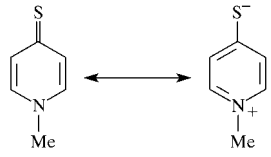


(IV*a*) R=CH_2COOH
(IV*b*) R=COOH

vinylogous analogues of thiolactams. Several papers deal with studies of dibenzo- and benzo-γ-pyridinethiones, *i.e.* derivatives of 9(10*H*)-acridinethione, (VI) (Jaud *et al.*, 1995), or 4(1*H*)-quinolinethione, (V) (Maslankiewicz *et al.*, 1998), respectively. This paper presents the data for the parent γ-pyridinethione, as exemplified by 1-methylpyridine-4(1*H*)-thione, (I).



The atom-numbering scheme is shown in Fig. 1, with selected bond lengths and angles given in Table 1. There are two symmetrically independent molecules in the unit cell which exhibit similar bond lengths and angles at the 2σ level. The pyridine rings of (I) are planar for both independent molecules [r.m.s. deviations of the ring atoms are 0.004 (3) and 0.005 (3) Å for molecules *A* and *B*, respectively]; *exo*-substituents S41*A*, C11*A* and S41*B* are in the planes of the appropriate rings within 3σ, except for C11*B* which deviates from the plane by 0.030 (4) Å. The two planar molecules are inclined at an angle of 67.75 (7)° with respect to one another. There is one intermolecular C—H···π interaction between molecules *A* and *B*, *viz*. C5*B*—H5*B*···*Cg*^{i} (*Cg* is the centroid of ring N1*A*/C2*A*/C3*A*/C4*A*/C5*A*/C6*A*), with an H···*Cg* distance of 2.69 Å [symmetry code: (i) $-1-x, 2-y, 1-z$].



(I) (I*a*)

The most interesting molecular feature of (I) is the planarity around the endocyclic N atom, indicating sp^2 hybridization of the N1 atom. Thus, the planar tricoordinated N1 atom should

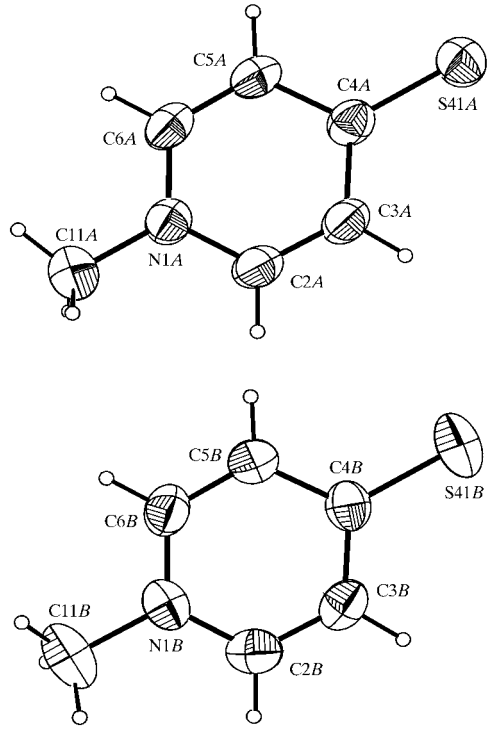


Figure 1
The molecular structures of the two symmetrically independent molecules of compound (I), with displacement ellipsoids at the 50% probability level.

[1] Part LXVI: Pluta *et al.* (2000).

bear a positive charge and, furthermore, a pyridinium-type resonance form (I*a*) should be the major contributor to the true molecular structure of (I)

It is well known (Witanowski *et al.*, 1973) that an N atom bearing a formal positive charge tends to produce a relatively sharp ^{14}N NMR signal. In fact, the ^{14}N NMR spectrum (in $CDCl_3$ solution) of the title compound reveals an N-atom signal at $\delta = -220$ p.p.m., with half-height of linewidths $\Delta\nu_{1/2} =$ 286 Hz (Zięba & Maslankiewicz, 1996). This has led to the conclusion that for compound (I), a pyridinium-type resonance form (I*a*) is the major contributor to the real molecular structure of (I). The occurrence of a positively charged endocyclic N atom should be accompanied by an elongation of the C—S bond of the thiocarbonyl group of (I*a*). However, the values of the endocyclic C—N—C bond angles of 118.7 (2) and 118.8 (2)° in (I) are below the generally accepted limit (120°; Pauling, 1960) for the endocyclic C—N—C bond angle in pyridinium salts.

Experimental

Compound (I) was synthesized and purified according to the method of Albert & Barlin (1959). Single crystals suitable for X-ray data collection were obtained on slow evaporation from an ethyl acetate solution.

Crystal data

C_6H_7NS
$M_r = 125.19$
Triclinic, $P\overline{1}$
$a = 7.544$ (1) Å
$b = 9.085$ (1) Å
$c = 9.302$ (1) Å
$\alpha = 89.84$ (1)°
$\beta = 84.03$ (1)°
$\gamma = 87.98$ (1)°
$V = 633.7$ (1) Å^3
$Z = 4$
$D_x = 1.312$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7$–19°
$\mu = 3.59$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.32 × 0.28 × 0.26 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
2861 measured reflections
2654 independent reflections
2012 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 78.2°$
$h = 0 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.135$
$S = 1.04$
2654 reflections
148 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0893P)^2 + 0.0559P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.018$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.012 (2)

H atoms were treated as riding atoms with *SHELXL*97 (Sheldrick, 1997) defaults, *i.e.* C—H = 0.93 Å for aromatic and 0.96 Å for methyl H atoms.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *SDP* (B. A. Frenz & Associates Inc., 1985); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Table 1
Selected geometric parameters (Å, °).

N1*A*—C6*A*	1.351 (3)	N1*B*—C2*B*	1.351 (3)
N1*A*—C2*A*	1.354 (3)	N1*B*—C6*B*	1.353 (3)
N1*A*—C11*A*	1.468 (3)	N1*B*—C11*B*	1.470 (3)
C2*A*—C3*A*	1.346 (3)	C2*B*—C3*B*	1.351 (3)
C3*A*—C4*A*	1.415 (3)	C3*B*—C4*B*	1.419 (3)
C4*A*—C5*A*	1.418 (3)	C4*B*—C5*B*	1.412 (3)
C4*A*—S41*A*	1.697 (2)	C4*B*—S41*B*	1.6922 (19)
C5*A*—C6*A*	1.352 (3)	C5*B*—C6*B*	1.350 (3)
C6*A*—N1*A*—C2*A*	118.71 (19)	C2*B*—N1*B*—C11*B*	121.2 (2)
C6*A*—N1*A*—C11*A*	121.21 (19)	C6*B*—N1*B*—C11*B*	120.0 (2)
C2*A*—N1*A*—C11*A*	120.07 (19)	N1*B*—C2*B*—C3*B*	121.77 (19)
C3*A*—C2*A*—N1*A*	121.57 (18)	C2*B*—C3*B*—C4*B*	121.76 (19)
C2*A*—C3*A*—C4*A*	122.11 (18)	C5*B*—C4*B*—C3*B*	113.95 (18)
C3*A*—C4*A*—C5*A*	114.18 (19)	C5*B*—C4*B*—S41*B*	122.90 (16)
C3*A*—C4*A*—S41*A*	123.53 (16)	C3*B*—C4*B*—S41*B*	123.14 (15)
C5*A*—C4*A*—S41*A*	122.29 (15)	C6*B*—C5*B*—C4*B*	122.29 (19)
C6*A*—C5*A*—C4*A*	121.52 (19)	C5*B*—C6*B*—N1*B*	121.40 (18)
C2*B*—N1*B*—C6*B*	118.80 (17)		

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1079). Services for accessing these data are described at the back of the journal.

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