C9—C4—C3	122.7 (3)	C17—C22—C21	119.4 (5)
C5—C4—C3	119.7 (4)	C28—C23—O2	116.8 (3)
C6—C5—C4	120.9 (4)	C28—C23—C24	121.1 (4)
C5—C6—C7	120.8 (4)	O2—C23—C24	122.1 (4)
C8—C7—C6	119.3 (4)	C23—C24—C25	116.6 (4)
C9—C8—C7	119.6 (5)	C26—C25—C24	122.5 (4)
C8—C9—C4	121.8 (4)	C25—C26—C27	119.6 (4)
N—C10—C11	115.1 (3)	C28—C27—C26	119.7 (4)
N—C10—S	110.2 (3)	C23—C28—C27	120.4 (4)
C11—C10—S	109.0 (3)		

All the crystals obtained were needle shaped and long. Crystals were fragile and so were not cut into smaller crystals.

The structure was solved by direct methods (*MULTAN*80; Main *et al.*, 1980) using *NRCVAX* (PC version) (Gabe, Le Page, Charland, Lee & White, 1989). H atoms, which were geometrically fixed and confirmed from difference Fourier maps, were used in the structure-factor calculations, but were not refined.

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4-*PC*. Data reduction: *NRCVAX*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971). Software used to prepare material for publication: *SHELXL*93.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: PA1239). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-[1-(Thiosemicarbazono)ethyl]pyridinium Chloride

Sonja Abram and Ulrich Abram

Universität Tübingen, Institut für Anorganische Chemie, Auf der Morgenstelle 18, D-72076 Tübingen, Germany. E-mail: ulrich.abram@uni-tuebingen.de

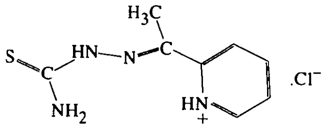
(*Received 16 September 1996; accepted 11 November 1996*)

Abstract

Dimeric units of the almost planar title compound, $C_8H_{11}N_4S^+.Cl^-$, are formed by N—H···Cl hydrogen bonds between the Cl^- anion and the H atom of the protonated pyridinium N atom, one H atom of the terminal NH_2 group of one thiosemicarbazone molecule and the second NH_2 H atom of a second molecule. The dimeric units are stacked in layers. The C—S bond length is 1.681 (3) Å and considerable double-bond character can be detected for the C—N bonds.

Comment

As part of our systematic studies on the coordination chemistry of indium(III) with tridentate ligands, we prepared the title compound, (I), which has been shown to form complexes with a variety of metal ions (Kovala-Demertzi, Domopoulou, Demertzis, Raptopoulou & Tertzis, 1994; Castineiras, West, Gebremedhin & Romack, 1994; West, Gebremedhin, Butcher & Jasinski, 1995). Complexes with thiosemicarbazone ligands are known to have considerable biological activity and are under discussion for medical purposes.



(I)

The title compound, (I), crystallizes as a chloride salt from ethanol solution. The N atom of the pyridine ring is protonated and the Cl^- anion is associated *via* hydrogen bonds to the H(1) and H(12*B*) atoms (Table 2). Another hydrogen bridge between the Cl^- anion and the H(12*A*) atom at $(-x, 1-y, 2-z)$ causes a slight association of every two molecules into dimeric units (Fig. 1). The title compound is almost planar [with a maximum deviation from the least-squares plane including all non-H atoms of 0.173 (1) Å and an r.m.s. deviation of 0.085 Å].

The C(11)—S(13) distance of 1.681 (3) Å is intermediate between typical C—S single- and double-bond lengths. This agrees well with the C(11)—N(10) and

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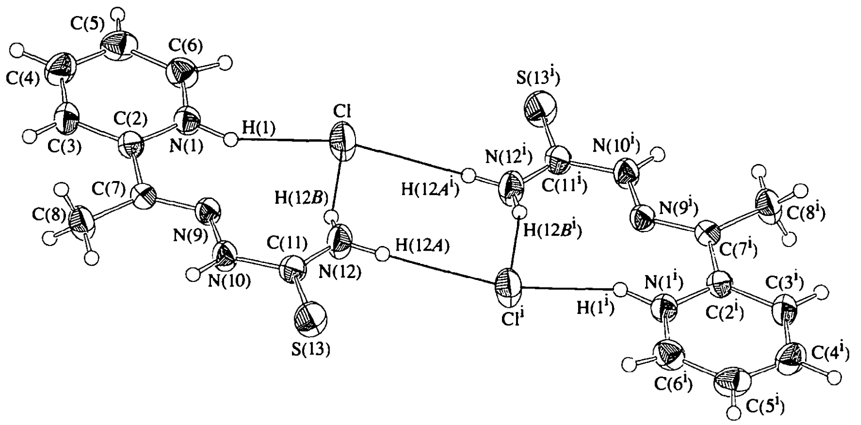

Fig. 1. *ZORTEP* diagram (Zsolnai, 1994) of the dimer of (I) showing 50% probability displacement ellipsoids. [Symmetry code: (i) $-x$, $1-y$, $2-z$.]

C(11)—N(12) bond lengths (Table 1) which indicate partial double-bond character. The C(7)—N(9) bond is significantly shorter than a C—N single bond, as can be expected for a thiosemicarbazone.

In summary, the bonding situation in the title compound, with considerable delocalization of electron density, makes the present results useful for the coordination chemistry of indium with which it should be able to form complexes as a neutral or monoanionic ligand according to the requirement of the metal (Abram, Maichle-Mössmer & Abram, 1997).

Experimental

2-[1-(Thiosemicarbazono)ethyl]pyridinium chloride was prepared by reacting equimolar amounts of 2-acetylpyridine and thiosemicarbazone hydrochloride in ethanol. The reaction mixture was heated under reflux for 2 h. After cooling, a pale yellow precipitate was formed which was recrystallized from boiling ethanol.

Crystal data

$C_8H_{11}N_4S^+.Cl^-$
$M_r = 230.72$
Monoclinic
$P2_1/n$
$a = 7.767$ (1) Å
$b = 7.882$ (1) Å
$c = 17.431$ (3) Å
$\beta = 100.93$ (2)°
$V = 1047.7$ (3) Å^3
$Z = 4$
$D_x = 1.463$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.76$–$15.43°$
$\mu = 0.53$ mm^{-1}
$T = 293$ (2) K
Plate
0.25 × 0.25 × 0.15 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none

$\theta_{max} = 25°$
$h = -9 \rightarrow 4$
$k = -9 \rightarrow 0$
$l = -20 \rightarrow 20$

1983 measured reflections
1811 independent reflections
1319 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0257$

3 standard reflections every 400 reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0381$
$wR(F^2) = 0.1032$
$S = 1.121$
1811 reflections
171 parameters
H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 0.2625P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.004$
$\Delta\rho_{max} = 0.245$ e Å^{-3}
$\Delta\rho_{min} = -0.222$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)* .

N(1)—C(6)	1.335 (3)	C(7)—N(9)	1.293 (3)
N(1)—C(2)	1.352 (3)	C(7)—C(8)	1.488 (4)
C(2)—C(3)	1.380 (4)	N(9)—N(10)	1.358 (3)
C(2)—C(7)	1.480 (3)	N(10)—C(11)	1.371 (3)
C(3)—C(4)	1.382 (4)	C(11)—N(12)	1.308 (4)
C(4)—C(5)	1.372 (5)	C(11)—S(13)	1.681 (3)
C(5)—C(6)	1.366 (4)		
N(1)—C(2)—C(7)	117.8 (2)	N(12)—C(11)—N(10)	117.5 (2)
N(9)—C(7)—C(2)	114.4 (2)	N(12)—C(11)—S(13)	124.7 (2)
C(7)—N(9)—N(10)	118.8 (2)	N(10)—C(11)—S(13)	117.8 (2)
N(9)—N(10)—C(11)	119.8 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D—H···A
N(1)—H(1)···Cl	0.93 (4)	2.19 (4)	150.1
N(12)—H(12B)···Cl	0.86 (3)	2.43 (3)	163.8
N(12)—H(12A)···Cl^i	0.87 (3)	2.62 (3)	155.5

Symmetry code: (i) $-x$, $1-y$, $2-z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL*93 and *HELENA* (Spek, 1994).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1422). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-Phenylsulfonyl-3-methylbenz[*f*]indole

T. Scott Yokum and Frank R. Fronczek

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA. E-mail: fronz@chxray1.chem.lsu.edu

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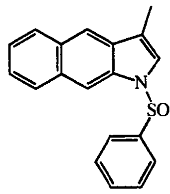
Abstract

In the title compound, $C_{19}H_{15}NO_2S$, the benz[*f*]indole ring system is essentially planar, with maximum and mean deviations for the 13 ring atoms of 0.051 (2) and 0.023 (4) Å. The N atom lies 0.199 (1) Å out of the plane of the three atoms bonded to it. The phenyl group forms a dihedral angle of 82.83 (5)° with the benz[*f*]indole plane. The S—N distance is 1.646 (1) Å and the S=O distances average 1.426 (1) Å.

Comment

Benz[*f*]tryptophan is of interest as a hybrid intrinsic/extrinsic fluorescence probe of peptide structure and dynamics. Tryptophan is a very useful intrinsic fluorescence probe and the additional benzannulation shifts the absorbance and emission to the red of tryptophan. In theory, benz[*f*]tryptophan could replace tryptophan in peptide hormones and retain the same or similar biological activity, while giving a unique fluorescence emission even in the presence of a protein receptor. The title molecule, (I), was synthesized as an intermediate to benz[*f*]tryptophan and has much greater oxidative stability compared with 2-trimethylsilyl-3-methylbenz[*f*]indole, which air oxidizes during recrystallization to form the hydroperoxide (Morales & Fronczek, 1996).



(I)

The N atom is slightly non-planar and lies 0.199 (1) Å out of the plane defined by the S, C1 and C4 atoms. This slight pyramidalization is similar to that seen in 1-phenylsulfonylindole [0.179 (1) Å] and similar compounds (Beddoes *et al.*, 1986). The conformation of the *N*-phenylsulfonyl group with respect to the ring system is described by torsion angles O1—S—N1—C4 of −54.5 (1)° and O1—S—C14—C19 of 19.2 (2)°, which cause the best planes of the benz[*f*]indole and phenyl rings to form a dihedral angle of 82.83 (5)°. The corresponding angles in 1-phenylsulfonylindole are −38.3,

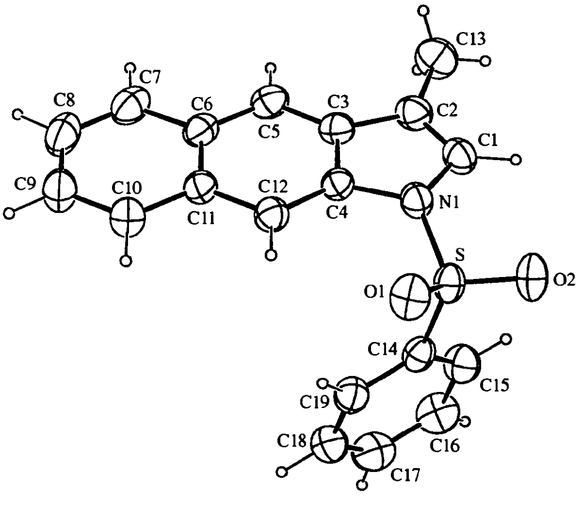


Fig. 1. The title molecule shown with ellipsoids at the 40% probability level and H atoms represented with arbitrary radii.

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