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1-[(1,3-Dihydro-2-benzothienyl)acetyl]-1*H*-indole *S*-oxide

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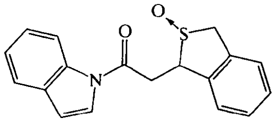
Abstract

The title compound, $C_{18}H_{15}NO_2S$, consists of two heterocycles, namely an indole and a 1,3-dihydro-2-benzothienyl *S*-oxide moiety, connected by an acetyl bridge. An S—O distance of 1.5007 (15) Å was observed and the two C—S distances differ, with S—CH_2 = 1.8217 (16) Å and S—CH = 1.8516 (16) Å.

Comment

The title compound, 1-[(1,3-dihydro-2-benzothienyl)-acetyl]-1*H*-indole *S*-oxide, (I), was synthesized according to a method reported previously (Bates & Xia, 1998). The present study was conducted in order to verify the assignment of relative stereochemistry assessed by ^{1}H NMR using aromatic solvent-induced shifts (Cooper *et al.*, 1969), and ^{1}H–^{1}H COSY (two-dimensional correlated spectroscopy) and NOE (nuclear Overhauser effect) difference spectra (Bates & Xia, 1998). The original assignments did agree with the general chromatographic order of elution observed for diastereomeric sulfoxides (Portoghese & Telang, 1971).



(I)

Compound (I) crystallized with one molecule constituting the asymmetric unit. An *ORTEP*-3 (Farrugia, 1997) representation of the molecule and the atom-labeling scheme are shown in Fig. 1. The bond lengths and valence angles are all within the ranges expected for this type of compound. The H atom on C11 is clearly *trans* to the O atom of the sulfoxide group, as was predicted in the earlier report (Bates & Xia, 1998). Note that the crystal consists of a racemic mixture of these compounds and the opposite configuration is present in the unit cell. The molecule is not planar and the two ring systems (*i.e.* the indole and the benzothienyl rings) are bent towards the sulfoxide group, with an angle of 13 (3)° between these two planes. This would appear to be the first reported X-ray structure of a 1,3-dihydro-2-benzothienyl *S*-oxide fragment (Allen & Kennard, 1993). An S—O distance of 1.5007 (15) Å was observed and the two C—S distances differ, with S1—C18 = 1.8217 (16) Å and S1—C11 = 1.8516 (16) Å.

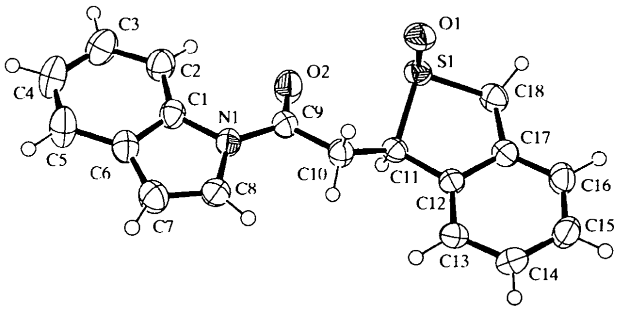


Fig. 1. View of (I) with ellipsoids at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

Experimental

Crystals of the title compound (m.p. 471–474 K) were prepared as described previously (Bates & Xia, 1998) and were crystallized slowly from an ethyl acetate solution.

Crystal data

$C_{18}H_{15}NO_2S$
M_r = 309.38
Monoclinic
$P2_1/c$
a = 4.963 (1) Å
b = 10.458 (2) Å
c = 28.310 (4) Å
β = 94.716 (16)°
V = 1464.4 (5) Å^3
Z = 4
D_x = 1.403 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 8.19–13.96°
μ = 0.228 mm^{-1}
T = 293 (2) K
Prism
0.20 × 0.20 × 0.18 mm
White

Data collection

Enraf–Nonius CAD-4 diffractometer

2802 reflections with $I > 2\sigma(I)$

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Non-profiled ω scans
Absorption correction:
ψ scan (North *et al.*, 1968)
$T_{min} = 0.936$, $T_{max} = 0.969$
3739 measured reflections
3355 independent reflections

$R_{int} = 0.012$
$\theta_{max} = 27.47°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 13$
$l = -36 \rightarrow 36$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.035$
$wR(F^2) = 0.104$
$S = 1.053$
3355 reflections
259 parameters
All H-atom parameters refined

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

A difference Fourier map indicated the possible locations of the H atoms. They were inserted as such and refined freely without constraint resulting in the final figures of merit for the compound. The C—H distances and U_{iso} values for the refined H atoms are in the ranges 0.91 (3)–1.01 (3) Å and 0.034 (4)–0.077 (7) Å^2, respectively.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*4 (Harms & Wocadlo, 1995). Program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997). Software used to prepare material for publication: *WinGX* (Farrugia, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1217). Services for accessing these data are described at the back of the journal.

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Hydrogen bonding in two piperidinium derivatives

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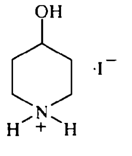
Abstract

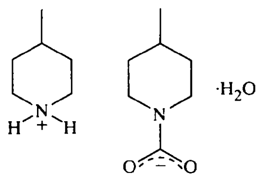
4-Hydroxypiperidinium iodide, $C_5H_{12}NO^+ \cdot I^-$, displays normal bond lengths and angles, but its crystal packing is unusual in involving four-centre hydrogen bonds from one NH group to two OH groups and one iodide anion as acceptors. 4-Methylpiperidinium 4-methylpiperidine-*N*-carboxylate hydrate, $C_6H_{14}N^+ \cdot C_7H_{12}NO_2^- \cdot H_2O$, is formed when 4-methylpiperidine absorbs CO_2 from the air. The N atom of the anion is essentially planar, in contrast to that in the parent amine. Four classical hydrogen bonds, one from each donor, are involved in forming broad layers of residues parallel to the *xy* plane.

Comment

We are interested in secondary interactions in various systems, *e.g.* in amine complexes of metals (Ahrens *et al.*, 1999) and in various amine derivatives (Jones & Ahrens, 1998; Freytag & Jones, 1999). We present here the structures of two piperidinium derivatives, namely 4-hydroxypiperidinium iodide, (1), and 4-methylpiperidinium 4-methylpiperidine-*N*-carboxylate hydrate, (2), one of which was obtained by chance.



(1)



(2)

4-Hydroxypiperidinium iodide, (1) (Fig. 1), displays the expected chair conformation of the cation, marginally flattened in the region of the N atom, with the hydroxy substituent equatorial. Bond lengths and angles may also be regarded as normal.

The crystal packing is largely determined by hydrogen bonding (Table 2); there are conventional, essentially linear, hydrogen bonds from N—H1′ (axial) and the OH group as donors to iodide as acceptor, with H···*A* distances similar to those of 2.76 and 2.55 Å, respectively, quoted by Steiner (1998) for normalized

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