Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1204). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(8R,8aS)-Indolizidine-1-spiro-2'-(1',3'-dithiane)-8-carbonitrile

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Abstract

The title compound, $C_{12}H_{18}N_2S_2$, is an indolizidine whose structure was determined unequivocally by X-ray diffraction. The indolizidine ring adopts a *trans*-fused envelope–chair conformation while the dithiane ring adopts a chair conformation distal to the nitrile moiety.

Comment

Numerous routes to the indolizidine ring system have been reported (for a recent example, see Carretero & Arrayas, 1995, and references therein), largely stimulated by their extremely potent inhibition of glycosidases (Elbein, 1987). Our synthesis of the indolizidine ring system stems from our ability to perform conjugate additions to unsaturated nitriles (Fleming & Pak, 1995) that serves to assemble rapidly heterocyclic indolizidines, quinolizidines (Hussain, Fleming, Norman & Chang, 1996) and azulenes.

The X-ray structure of the title compound, (I), shows that the indolizidine ring system adopts the envelope–chair orientation found in both the crystalline state (Koh, Lee, Sim & Zhu, 1993) and in solution (Reymond, Pinkerton & Vogel, 1991). The metric parameters of the rings are quite similar to the indolizidine 1-deoxy-castanospermine (Koh, Lee, Sim & Zhu, 1993) and, in the present case, differ mainly in the shortening of the N(1)—C(9) bond [1.459 (4) *versus* 1.479 (5) Å] and lengthening of C(7)—C(8) [1.550 (4) *versus* 1.522 (5) Å] and C(8)—C(9) [1.528 (4) *versus* 1.514 (5) Å]. A similar though less-pronounced trend is seen in the homologous quinolizine (Hussain, Fleming, Norman & Chang, 1996).

(I)
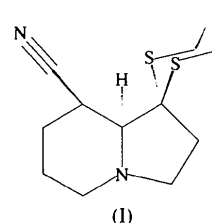
The exact reason for these trends are unclear though we may explain this phenomenon by an interaction between the electron-rich N atom and the strongly electron-withdrawing nitrile group (Reddy, Goldstein &
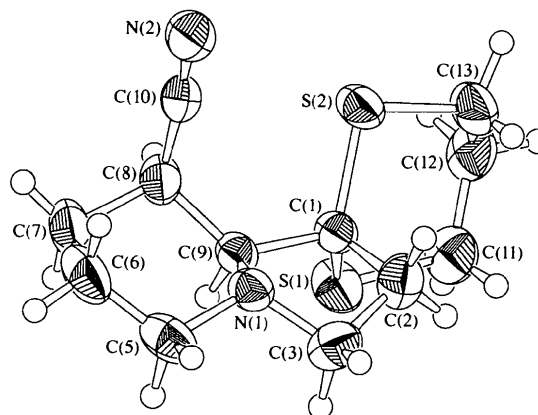

Fig. 1. Perspective drawing of (8R,8aS)-indolizidine-1-spiro-2'-(1',3'-dithiane)-8-carbonitrile with displacement ellipsoids drawn at the 50% probability level.

Mandell, 1961). There is a good precedent for this type of interaction in α-cyanoamines as it is manifest in the facile elimination of cyanide (Yue, Royer & Husson, 1992), but prior difficulties in synthesizing β-cyanoamines may have precluded this effect from being observed previously.

Experimental

The synthesis of the title compound follows our earlier preparation (Hussain, Fleming, Norman & Chang, 1996) of the homologous octahydroquinolizine. Recrystallization from hot hexane afforded a crystalline material from which a single crystal was selected for diffraction.

Crystal data

$C_{12}H_{18}N_2S_2$	Mo $K\alpha$ radiation
$M_r = 254.41$	$\lambda = 0.7107$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 10.513(3)$ Å	$\theta = 16.81–20.50°$
$b = 11.182(2)$ Å	$\mu = 0.367$ mm^{-1}
$c = 11.206(2)$ Å	$T = 294$ K
$\beta = 97.18(2)°$	Triangular pyramid
$V = 1307.0(5)$ Å^3	$0.35 \times 0.30 \times 0.30$ mm
$Z = 4$	White
$D_x = 1.293$ Mg m^{-3}	
D_m not measured	

Data collection

AFC-7R diffractometer	$R_{int} = 0.044$
$\omega/2\theta$ scans	$\theta_{max} = 32.50°$
Absorption correction:	$h = 0 \rightarrow 14$
ψ scans (TEXSAN;	$k = 0 \rightarrow 15$
Molecular Structure	$l = -15 \rightarrow 15$
Corporation, 1992)	3 standard reflections
$T_{min} = 0.83$, $T_{max} = 0.90$	monitored every 150
4997 measured reflections	reflections
4787 independent reflections	intensity decay: -1.8%
2248 observed reflections	
$[I > 3.00\sigma(I)]$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.124$
$R = 0.060$	$\Delta\rho_{max} = 0.61$ e Å^{-3}
$wR = 0.076$	$\Delta\rho_{min} = -0.55$ e Å^{-3}
$S = 1.92$	Extinction correction: none
2248 reflections	Atomic scattering factors
217 parameters	from *International Tables*
All H-atom parameters	*for X-ray Crystallography*
refined	(1974, Vol. IV)
$w = 4F^2/\sigma^2(F^2)$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
S(1)	0.46482(9)	0.06809(8)	0.17378(8)	0.0599(3)
S(2)	0.3473(1)	0.30739(7)	0.21052(7)	0.0576(2)
N(1)	0.2379(2)	0.1821(2)	-0.0841(2)	0.0453(7)
N(2)	0.2944(4)	0.5086(3)	-0.0264(3)	0.072(1)
C(1)	0.3390(3)	0.1726(2)	0.1189(2)	0.0413(7)
C(2)	0.2042(4)	0.1156(4)	0.1047(3)	0.059(1)
C(3)	0.1804(4)	0.0818(3)	-0.0276(3)	0.060(1)
C(5)	0.2497(4)	0.1668(4)	-0.2119(3)	0.061(1)
C(6)	0.3143(4)	0.2742(4)	-0.2582(3)	0.069(1)
C(7)	0.4413(4)	0.3024(4)	-0.1835(3)	0.066(1)
C(8)	0.4246(3)	0.3140(3)	-0.0484(3)	0.0481(9)
C(9)	0.3627(3)	0.1978(3)	-0.0129(2)	0.0417(7)
C(10)	0.3495(3)	0.4214(3)	-0.0323(3)	0.0510(9)
C(11)	0.4404(5)	0.0470(4)	0.3295(3)	0.064(1)
C(12)	0.4426(4)	0.1601(4)	0.4016(3)	0.063(1)
C(13)	0.3342(5)	0.2433(4)	0.3574(3)	0.064(1)

Table 2. *Selected geometric parameters (Å, °)*

S(1)—C(1)	1.814(3)	C(1)—C(9)	1.555(4)
S(1)—C(11)	1.810(4)	C(2)—C(3)	1.520(5)
S(2)—C(1)	1.820(3)	C(5)—C(6)	1.503(6)
S(2)—C(13)	1.816(3)	C(6)—C(7)	1.518(6)
N(1)—C(3)	1.456(4)	C(7)—C(8)	1.550(4)
N(1)—C(5)	1.463(4)	C(8)—C(9)	1.528(4)
N(1)—C(9)	1.459(4)	C(8)—C(10)	1.462(5)
N(2)—C(10)	1.140(4)	C(11)—C(12)	1.500(6)
C(1)—C(2)	1.544(5)	C(12)—C(13)	1.506(6)
C(1)—S(1)—C(11)	103.0(2)	N(1)—C(5)—C(6)	110.0(3)
C(1)—S(2)—C(13)	100.4(2)	C(5)—C(6)—C(7)	112.3(3)
C(3)—N(1)—C(5)	115.2(3)	C(6)—C(7)—C(8)	110.9(3)
C(3)—N(1)—C(9)	104.4(2)	C(7)—C(8)—C(9)	106.7(3)
C(5)—N(1)—C(9)	111.6(3)	C(7)—C(8)—C(10)	108.6(3)
S(1)—C(1)—S(2)	111.2(2)	C(9)—C(8)—C(10)	114.4(3)
S(1)—C(1)—C(2)	113.0(2)	N(1)—C(9)—C(1)	104.9(2)
S(1)·· C(1)—C(9)	104.0(2)	N(1)—C(9)—C(8)	110.1(2)
S(2)—C(1)—C(2)	112.3(2)	C(1)—C(9)—C(8)	121.7(2)
S(2)—C(1)—C(9)	112.6(2)	N(2)—C(10)—C(8)	175.2(3)
C(2)—C(1)—C(9)	103.4(2)	S(1)—C(11)—C(12)	114.5(3)
C(1)—C(2)—C(3)	103.9(3)	C(11)—C(12)—C(13)	112.6(3)
N(1)—C(3)—C(2)	101.9(3)	S(2)—C(13)—C(12)	113.7(3)

The C—H bonds range from 0.89(3) to 1.07(4) Å and the H-atom displacement parameters from 0.043(8) to 0.10(1) Å^2.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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The compound crystallizes with no short intermolecular contacts. A perspective view of a single molecule is shown in Fig. 1.

9-Dicyclohexylphenylphosphino-*arachno*-6-thiadecaborane(11)

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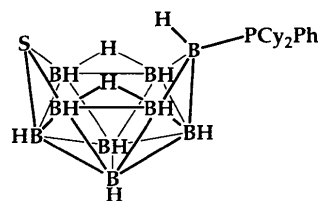
Abstract

The {SB$_9$} cage residue in the title compound, C$_{18}$H$_{38}$B$_9$PS, has the expected *arachno* ten-vertex geometry and the PCy$_2$Ph substituent occupies an *exo* position on B9, with B9—P1 = 1.953 (6) Å.

Comment

There is current interest in bis(phosphine)rhodathiaboranes whose molecular structures appear to be at variance with those expected by electron-counting rules (Ferguson *et al.*, 1990; Murphy, Spalding, Ferguson & Gallagher, 1992) unless intramolecular agostic interactions are invoked (Adams, McGrath & Welch, 1995; Adams, McGrath, Thomas, Weller & Welch, 1996). As part of our studies in this area, we attempted the synthesis of 8,8-(Cy$_2$PhP)$_2$-8,7-*nido*-RhSB$_9$H$_{10}$ (Cy = cyclohexyl) by reaction between [RhCl(PCy$_2$Ph)$_2$(C$_2$H$_4$)], generated *in situ* from [RhCl(C$_2$H$_4$)$_2$]$_2$ and PCy$_2$Ph, and Cs[SB$_9$H$_{12}$] in Et$_2$O. However, the major tractable product afforded by work-up proved to be the title compound. Since there is current interest in 9-substituted *arachno*-6-SB$_9$H$_{11}$ species (Stibr *et al.*, 1996) and since 9-PPh$_3$-*arachno*-6-SB$_9$H$_{11}$ has been variously described (by the same workers) as *endo*-9- (Nestor, Fontaine, Greenwood, Kennedy & Thornton-Pett, 1991) and *exo*-9- (Stibr *et al.*, 1996), we undertook a crystallographic study of the title compound.
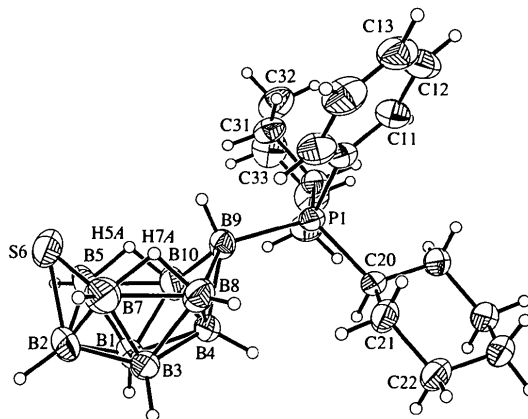

Fig. 1. Perspective view with 40% ellipsoids for non-H atoms. Ring C atoms are numbered in sequence.

This is the first crystallographic characterization of a 9-phosphino-6-SB$_9$H$_{11}$ species. The {SB$_9$} residue has the same basic *arachno* structure as that found in 9-NEt$_3$-*arachno*-6-SB$_9$H$_{11}$ (Hilty & Rudolf, 1979), [*arachno*-6-SB$_9$H$_{12}$]$^-$ (Nestor *et al.*, 1991) and 9-MeCN-*arachno*-6-SB$_9$H$_{11}$ (Stibr *et al.*, 1996). Similar to the situation in all these three analogous compounds, the B—B distances in the title compound appear to fall into three fairly distinct groups: *ca* 1.90 Å for B2—B5, B2—B7, B8—B9 and B9—B10; *ca* 1.85 Å for the hydrogen-bridged edges B5—B10 and B7—B8; *ca* 1.75–1.80 Å for all others. S—B distances in the title compound are comparable with those in the thiaboranes referenced above, but more spread than usual with S6—B2 being just significantly longer than S6—B5 and S6—B7.

Overall, the thiaborane cage has approximate C_s symmetry about the plane through S6, B2, B4 and B9, and the ^{11}B NMR spectrum is fully consistent with such symmetry in solution. However, it is clear from Fig. 1 that the PCy$_2$Ph substituent at B9 [which is clearly in an *exo* position, B9—P1 1.953 (6) Å] is not oriented so as to maintain overall C_s symmetry in the solid state. We assume that in solution at room temperature, the PCy$_2$Ph ligand is free to rotate about the B9—P1 bond.

Experimental

Under an atmosphere of dry nitrogen, a solution of [RhCl(PCy$_2$Ph)$_2$(C$_2$H$_4$)] in Et$_2$O was prepared *in situ* by slow