Influence of the Coordination Number of Nitrogen on the Structure of $6a\lambda^4$-Thia-1,3,4,6-tetraazapentalenic Systems. Crystal Structure Analyses of 3-(2-Pyridylimino)-3*H*-[1,2,4]thiadiazolo[4,3-*a*]pyridine and its 1-Methylated Salt

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Structural data were obtained by X-ray crystallography for the title compounds which show that they are essentially planar and exhibit an approximately linear N2-S1-N8 arrangement. In compound **3** the separation between the sulfur atom and the pyridine nitrogen atom (2.61 Å) is larger than the Huggins constant energy distance (2.58 Å), suggesting that there is little or no bonding between them. The methylated salt **4**, on the contrary, has a closer S...N(pyridine) distance (2.19 Å) with an estimated bond dissociation energy of 6 kcal/mole.

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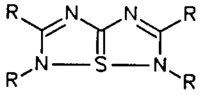
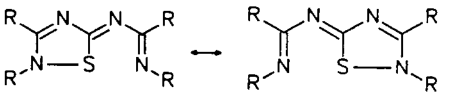
The popularity of $6a\lambda^4$-thiapentalenes and related molecules as targets for X-ray crystallographic studies is due to their unusual structural and bonding properties [1]. For instance, in $6a\lambda^4$-thia-1,3,4,6-tetraazapentalenes **1** the colinear heteroatom unit N-S-N is involved in a four-electron three-center system. The S-N bonds are distinctly longer than the normal covalent bond (1.74 Å), but much shorter than the sum of the van der Waals radii for sulfur and nitrogen (3.35 Å) [2]. The molecules are best represented by the dual canonical forms **1a** and **1b**, which indicate single bond/no bond resonance, as well as π-delocalization embracing all the nitrogen and carbon atoms.

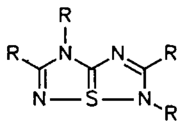


1



1a **1b**

The terminal three-coordinated nitrogen atoms in the conventional representation **1** have doubly occupied p_z orbitals available for p_π-p_π conjugation with the neighboring ring atoms. A structural variation is provided by **2** where one of the nitrogen atoms of the N-S-N sequence is dicoordinated and, hence, contributes a singly occupied p_z orbital to the ring conjugation. Since such a molecule can be drawn in only one open-chain resonance structure **2a**, we expect the S...NR bond to be weaker than in **1**. No crystallographic information, however, is available.



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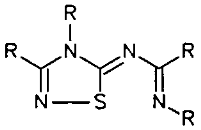
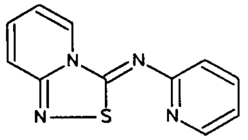
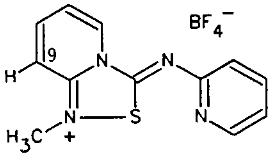


2a

A compound which meets the requirements for structure **2** is the reported [1,2,4]thiadiazolo[4,3-*a*]pyridine **3**, prepared by Potts and Armbruster [3] from 2-aminopyridine and perchloromethyl mercaptan. We have prepared this compound following the reported procedure, and compared its crystal structure with that of the methylated salt **4**.



3



4

That methylation of **3** with Meerwein's reagent occurred at the thiadiazole N-2 position was deduced from the nmr spectrum by a homonuclear double resonance NOE experiment. Thus, presaturation of the methyl resonance at δ 3.7 caused a 14% enhancement of the H-9 signal intensity at δ 7.8. The ^{1}H and ^{13}C nmr data are summarized in Table 1. Assignment of the peaks was based on the observed multiplicity in the coupled spectra, and 2D ^{1}H,^{13}C one-bond correlation. From Table 1 we conclude that methylation of **3** affects all proton and carbon nmr absorptions of the molecule, so that the chemical shifts cannot be used for locating the methyl substituent.

The molecular structures of **3** and **4** are shown in Figures 1 and 2. The molecules are quasi planar, with a

Table 1

NMR Chemical Shifts of the Heterocycles [a]

	Compound **3**		Compound **4**	
C,H [b]	^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR
3		146.9		147.4
5		162.6		155.2
7		157.0		151.8
9	7.2	119.4	7.80	111.8
10	7.2	132.0	8.16	141.6
11	6.55	110.1	7.30	113.7
12	8.5	126.2	9.0	127.7
13	7.4	119.8	7.90	120.7
14	7.7	137.5	8.22	140.7
15	6.95	116.5	7.55	120.1
16	8.55	145.3	8.94	139.1
17			3.7	30.9

[a] The nmr spectra (δ-values in ppm from TMS) were recorded on a Bruker spectrometer, operating at 400 MHz (^{1}H) and 100 MHz (^{13}C). The standard Bruker pulse program hxco was used for the 2D heteronuclear correlation experiments. Solvents used were deuteriochloroform for **3** and dimethyl sulfoxide-d$_6$ for **4**. [b] The arbitrary numbering used is shown in Figures 1 and 2.

Table 2

Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 x 10^3)* of Compound **3**

	x	y	z	U(eq)
S(1)	2786(1)	1731(1)	1130(1)	43(1)
N(2)	1809(4)	2912(2)	536(2)	45(1)
C(3)	3243(4)	3263(2)	-45(2)	38(1)
N(4)	5206(3)	2639(2)	-45(1)	33(1)
C(5)	5276(4)	1696(2)	574(2)	34(1)
N(6)	6940(3)	1011(2)	629(2)	37(1)
C(7)	6864(4)	81(2)	1255(2)	35(1)
N(8)	5124(4)	-12(2)	1795(2)	41(1)
C(9)	3028(5)	4216(3)	-694(2)	45(1)
C(10)	4668(5)	4459(3)	-1262(2)	49(1)
C(11)	6646(5)	3809(3)	-1223(2)	47(1)
C(12)	6905(5)	2915(3)	-621(2)	40(1)
C(13)	8576(5)	-717(3)	1297(2)	38(1)
C(14)	8473(5)	-1636(3)	1907(2)	42(1)
C(15)	6683(5)	-1748(3)	2468(2)	44(1)
C(16)	5076(5)	-923(3)	2380(2)	45(1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

mean deviation of 0.017 Å for **3** and 0.006 Å for **4** from the best plane through the eight atoms 1-8. The N1 atom in **4** has no pyramidal character since it lies only 0.002 Å out of the plane through its neighbors S1, C3 and C17. The N2-S1-N8 angles, 165.9° for **3** and 164.4° for **4**, approach the linear arrangement predicted to be the most favorable for electron-rich three-center bonds.

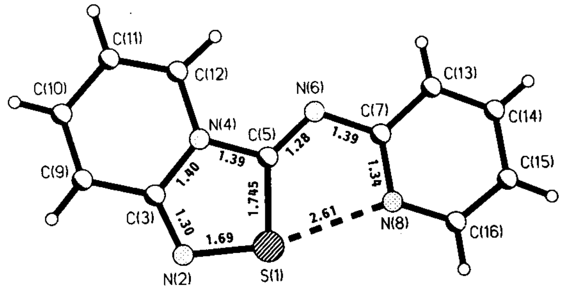


Figure 1. Molecular structure of **3** with arbitrary numbering scheme and selected bond lengths

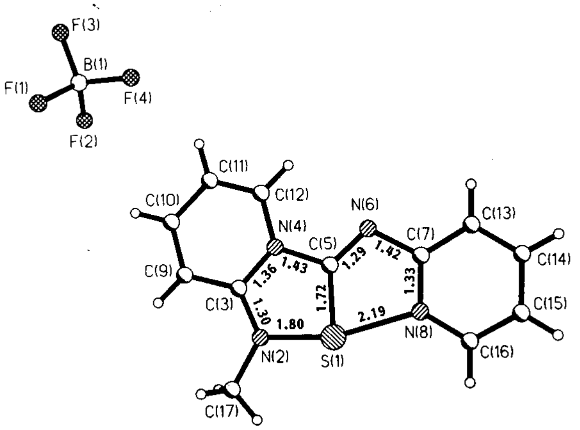
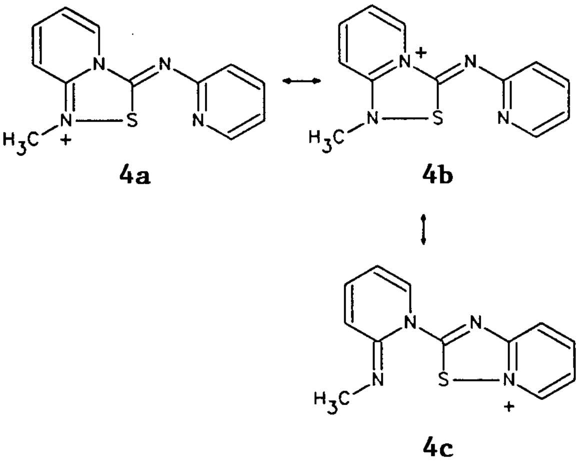


Figure 2. Molecular structure of **4** with arbitrary numbering scheme and selected bond lengths

Molecule **3** shows a normal S1-N2 bond length (1.69 Å) for thiadiazoles [4] and a S1...N8 distance (2.61 Å) which is shorter than the sum of the corresponding van der Waals radii (3.35 Å). The transformation of **3** into its methylated salt **4** results in a stretching of the S1-N2 bond (1.80 Å) and a marked shortening of the S1...N8 distance (2.19 Å). Thus, **4** is best expressed by the canonical forms **4a** and **4b** and to a much lesser extend by **4c**.

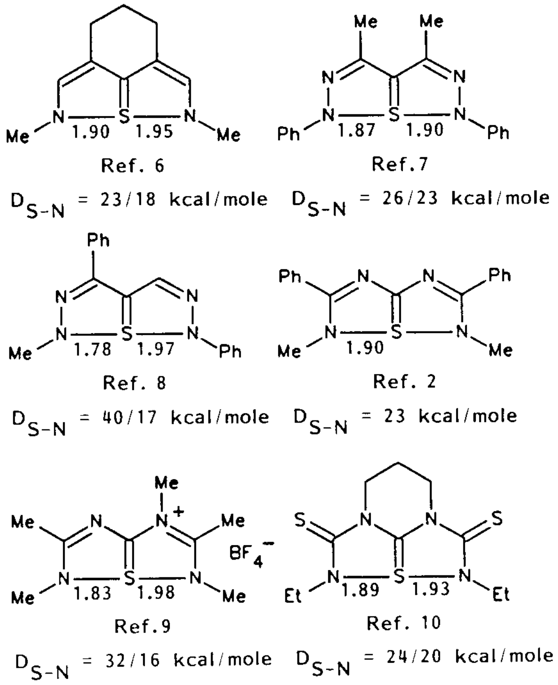


In order to estimate the covalent bond strength of S1...N8, Huggins' equation (1) can be used [5]:

$$D_{AB} = 10^{2(r_A^* + r_B^* - r_{AB})} \qquad (1)$$

where D_{AB} is the bond dissociation energy in kcal/mole, r_{AB} is the observed bond distance, and r_A^* and r_B^* are the computed constant energy radii for the atoms A and B, respectively. In the case of **4**, the S1...N8 distance is significantly less than the Huggins constant energy distance of 2.58 Å, and the calculated dissociation energy of 6 kcal/mole indicates a weak covalent bond. For comparison, the bond dissociation energies of some other thiapentalenes with a N-S-N structural unit were calculated, and the results are shown in Scheme 1.

Scheme 1



Compound **3** has an S1...N8 separation of 2.61 Å, slightly larger than the Huggins constant energy distance of 2.58 Å. Hence, this does not reflect a covalent bonding (< 1 kcal/mole), but rather a weakly interacting contact sufficient to hold the molecule in the observed conformation.

EXPERIMENTAL

1-Methyl-3-(2-pyridylimino)-3*H*-[1,2,4]thiadiazolo[4,3-*a*]pyridinium Tetrafluoroborate (4).

A solution of **3** (0.42 g, 1.8 mmoles) [3] and trimethyloxonium tetrafluoroborate (0.29 g, 2 mmoles) in dichloromethane (20 ml) was stirred overnight at 5°. After cooling at −20° for one day, **4** crystallized out in 66% yield (0.29 g), mp 232° (twice from ethanol).

Table 3

Bond Lengths (Å) of Compound **3**

S(1)-N(2)	1.690(2)	S(1)-C(5)	1.745(3)
N(2)-C(3)	1.296(4)	C(3)-N(4)	1.396(3)
C(3)-C(9)	1.432(4)	N(4)-C(5)	1.393(3)
N(4)-C(12)	1.388(4)	C(5)-N(6)	1.284(3)
N(6)-C(7)	1.392(3)	C(7)-N(8)	1.343(3)
C(7)-C(13)	1.388(4)	N(8)-C(16)	1.337(4)
C(9)-H(9)	0.972(31)	C(9)-C(10)	1.344(5)
C(10)-H(10)	0.940(32)	C(10)-C(11)	1.418(5)
C(11)-H(11)	0.972(30)	C(11)-C(12)	1.341(4)
C(12)-H(12)	1.009(28)	C(13)-H(13)	0.912(27)
C(13)-C(14)	1.367(4)	C(14)-H(14)	0.909(29)
C(14)-C(15)	1.388(4)	C(15)-H(15)	0.975(31)
C(15)-C(16)	1.363(4)	C(16)-H(16)	0.944(28)

Table 4

Bond Angles (°) of Compound **3**

N(2)-S(1)-C(5)	95.0(1)	S(1)-N(2)-C(3)	109.5(2)
N(2)-C(3)-N(4)	116.5(2)	N(2)-C(3)-C(9)	127.1(3)
N(4)-C(3)-C(9)	116.4(2)	C(3)-N(4)-C(5)	113.5(2)
C(3)-N(4)-C(12)	123.2(2)	C(5)-N(4)-C(12)	123.2(2)
S(1)-C(5)-N(4)	105.4(2)	S(1)-C(5)-N(6)	133.6(2)
N(4)-C(5)-N(6)	120.9(2)	C(5)-N(6)-C(7)	117.3(2)
N(6)-C(7)-N(8)	118.5(2)	N(6)-C(7)-C(13)	119.0(2)
N(8)-C(7)-C(13)	122.5(2)	C(7)-N(8)-C(16)	117.3(2)
C(3)-C(9)-H(9)	116.0(18)	C(3)-C(9)-C(10)	119.7(3)
H(9)-C(9)-C(10)	124.2(18)	C(9)-C(10)-H(10)	121.9(19)
C(9)-C(10)-C(11)	121.6(3)	H(10)-C(10)-C(11)	116.5(19)
C(10)-C(11)-H(11)	121.6(18)	C(10)-C(11)-C(12)	120.2(3)
H(11)-C(11)-C(12)	118.2(18)	N(4)-C(12)-C(11)	118.8(3)
N(4)-C(12)-H(12)	113.9(16)	C(11)-C(12)-H(12)	127.2(16)
C(7)-C(13)-H(13)	120.0(17)	C(7)-C(13)-C(14)	118.5(3)
H(13)-C(13)-C(14)	121.5(17)	C(13)-C(14)-H(14)	120.4(18)
C(13)-C(14)-C(15)	119.8(3)	H(14)-C(14)-C(15)	119.8(18)
C(14)-C(15)-H(15)	120.9(18)	C(14)-C(15)-C(16)	117.7(3)
H(15)-C(15)-C(16)	121.3(18)	N(8)-C(16)-C(15)	124.2(3)
N(8)-C(16)-H(16)	116.4(17)	C(15)-C(16)-H(16)	119.4(17)

Anal. Calcd. for $C_{12}H_{11}BF_4N_4S$ (mol wt 329.9): C, 43.68; H, 3.38. Found: C, 43.60; H, 3.50.

Crystal Structure Analysis of 3.

Compound **3** crystallized from acetone in the space group $P2_1/n$ with a = 6.112(1), b = 11.440(2), c = 14.266(2) Å, β = 92.41(1)°, V = 996.7(2) Å^3, Z = 4, D_x = 1.521 gcm^{-3}. Intensities from a red prismatic crystal 0.3 x 0.3 x 0.3 mm were measured using a Siemens P4-PC diffractometer with graphite-monochromatized CuKα-radiation (λ = 1.54178 Å). Of the 1365 independent reflections with $\sin\theta/\lambda \leq 0.55$ Å^{-1}, 1288 had F > 4.0 σ(F) and were considered as observed. The structure was solved by direct methods and refined by full-matrix least-squares methods [11] to an R-value of 0.031 for the observed reflections. Atomic coordinates, bond lengths and angles are given in Tables 2, 3 and 4. Figure 1 shows the molecule with selected bond lengths.

Table 5

Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 x 10^3)* of Compound **4**

	x	y	z	U(eq)
S(1)	2146(2)	709(1)	4293(1)	52(1)
N(2)	2395(6)	1980(4)	4889(2)	53(2)
C(3)	2718(7)	1623(5)	5517(3)	46(2)
N(4)	2777(6)	348(4)	5589(2)	47(2)
C(5)	2514(7)	-313(5)	4964(3)	45(2)
N(6)	2533(6)	-1521(4)	4977(2)	50(2)
C(7)	2252(8)	-1990(5)	4309(3)	52(2)
N(8)	1951(6)	-1145(4)	3818(2)	48(2)
C(9)	2977(8)	2378(5)	6102(3)	57(2)
C(10)	3259(8)	1783(6)	6713(3)	60(2)
C(11)	3306(8)	461(6)	6769(3)	62(2)
C(12)	3084(7)	-242(5)	6204(3)	51(2)
C(13)	2207(9)	-3281(5)	4177(3)	63(2)
C(14)	1886(9)	-3664(6)	3520(3)	70(3)
C(15)	1595(9)	-2779(6)	3015(3)	68(2)
C(16)	1642(8)	-1525(6)	3170(3)	61(2)
C(17)	2225(10)	3270(5)	4652(3)	72(3)
B(1)	1743(13)	950(7)	8543(4)	70(3)
F(1)	95(8)	1719(5)	8477(2)	136(2)
F(2)	3288(7)	1636(5)	8372(2)	138(2)
F(3)	2180(7)	528(3)	9189(2)	106(2)
F(4)	1307(7)	-30(3)	8102(2)	104(2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 6

Bond Lengths (Å) of Compound **4**

S(1)-N(2)	1.797(4)	S(1)-C(5)	1.720(5)
S(1)-N(8)	2.186(4)	N(2)-C(3)	1.303(7)
N(2)-C(17)	1.451(7)	C(3)-N(4)	1.364(7)
C(3)-C(9)	1.411(8)	N(4)-C(5)	1.426(6)
N(4)-C(12)	1.372(6)	C(5)-N(6)	1.286(7)
N(6)-C(7)	1.418(7)	C(7)-N(8)	1.327(7)
C(7)-C(13)	1.397(8)	N(8)-C(16)	1.346(7)
C(9)-H(9)	0.960	C(9)-C(10)	1.368(8)
C(10)-H(10)	0.960	C(10)-C(11)	1.411(9)
C(11)-H(11)	0.960	C(11)-C(12)	1.348(8)
C(12)-H(12)	0.960	C(13)-H(13)	0.960
C(13)-C(14)	1.366(8)	C(14)-H(14)	0.960
C(14)-C(15)	1.374(9)	C(15)-H(15)	0.960
C(15)-C(16)	1.369(9)	C(16)-H(16)	0.960
C(17)-H(171)	0.960	C(17)-H(172)	0.960
C(17)-H(173)	0.960	B(1)-F(1)	1.365(10)
B(1)-F(2)	1.355(10)	B(1)-F(3)	1.361(8)
B(1)-F(4)	1.369(8)		

Crystal Structure Analysis of 4.

Compound **4** crystallized from ethanol in the space group $P2_1/n$ with $a = 6.712(1)$, $b = 10.636(2)$, $c = 20.108(4)$ Å, $\beta = 99.26(1)°$, $V = 1416.7(5)$ Å^3, $Z = 4$, $D_x = 1.548$ gcm^{-3}. Intensities from a yellow needle with dimensions 0.3 x 0.1 x 0.1 mm were measured using a Siemens P4-PC diffractometer with graphite-monochromatized CuKα radiation ($\lambda = 1.54178$ Å). Of the 1927 independent reflections with $\sin \theta/\lambda \leq 0.55$ Å^{-1}, 1409 had $F > 4.0\ \sigma(F)$ and were considered as observed. The structure was solved by direct methods and refined by full-matrix least-squares methods [11] to an R-value of 0.052 for the observed reflections. Atomic coordinates, bond lengths and angles are given in Tables 5, 6 and 7. Figure 2 shows the molecule with selected bond lengths.

Table 7

Bond Angles (°) of Compound **4**

N(2)-S(1)-C(5)	88.0(2)	N(2)-S(1)-N(8)	164.4(2)
C(5)-S(1)-N(8)	76.4(2)	S(1)-N(2)-C(3)	114.2(4)
S(1)-N(2)-C(17)	119.9(4)	C(3)-N(2)-C(17)	125.9(4)
N(2)-C(3)-N(4)	113.0(4)	N(2)-C(3)-C(9)	128.4(5)
N(4)-C(3)-C(9)	118.7(5)	C(3)-N(4)-C(5)	113.5(4)
C(3)-N(4)-C(12)	123.2(4)	C(5)-N(4)-C(12)	123.2(4)
S(1)-C(5)-N(4)	111.3(3)	S(1)-C(5)-N(6)	130.3(4)
N(4)-C(5)-N(6)	118.4(4)	C(5)-N(6)-C(7)	109.5(4)
N(6)-C(7)-N(8)	116.6(5)	N(6)-C(7)-C(13)	121.4(5)
N(8)-C(7)-C(13)	121.9(5)	S(1)-N(8)-C(7)	107.1(3)
S(1)-N(8)-C(16)	133.0(4)	C(7)-N(8)-C(16)	119.8(5)
C(3)-C(9)-H(9)	121.2(3)	C(3)-C(9)-C(10)	117.8(5)
H(9)-C(9)-C(10)	121.1(3)	C(9)-C(10)-H(10)	118.9(3)
C(9)-C(10)-C(11)	122.0(5)	H(10)-C(10)-C(11)	119.1(3)
C(10)-C(11)-H(11)	120.4(3)	C(10)-C(11)-C(12)	119.2(5)
H(11)-C(11)-C(12)	120.4(3)	N(4)-C(12)-C(11)	119.1(5)
N(4)-C(12)-H(12)	120.5(3)	C(11)-C(12)-H(12)	120.4(3)
C(7)-C(13)-H(13)	121.1(3)	C(7)-C(13)-C(14)	118.1(5)
H(13)-C(13)-C(14)	120.8(4)	C(13)-C(14)-H(14)	120.2(4)
C(13)-C(14)-C(15)	119.4(6)	H(14)-C(14)-C(15)	120.4(4)
C(14)-C(15)-H(15)	119.7(4)	C(14)-C(15)-C(16)	120.2(6)
H(15)-C(15)-C(16)	120.0(3)	N(8)-C(16)-C(15)	120.4(5)
N(8)-C(16)-H(16)	119.8(3)	C(15)-C(16)-H(16)	119.8(3)
N(2)-C(17)-H(171)	109.5(3)	N(2)-C(17)-H(172)	109.5(3)
H(171)-C(17)-H(172)	109.5(1)	N(2)-C(17)-H(173)	109.5(3)
H(171)-C(17)-H(173)	109.5(1)	H(172)-C(17)-H(173)	109.5(1)
F(1)-B(1)-F(2)	107.1(6)	F(1)-B(1)-F(3)	109.6(6)
F(2)-B(1)-F(3)	111.3(6)	F(1)-B(1)-F(4)	108.0(6)
F(2)-B(1)-F(4)	109.8(6)	F(3)-B(1)-F(4)	110.9(6)

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