

6aλ⁴-Thia-1,2,3,4,6-pentaazapentalene

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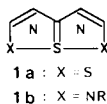
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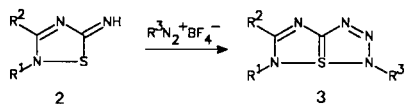
6aλ⁴-Thia-1,2,3,4,6-pentaazapentalenes **3** are conveniently prepared by reacting 5-imino-Δ³-1,2,4-thiadiazolines **2** with aromatic diazonium tetrafluoroborates in the presence of pyridine. The first crystal structure analysis of this class of compounds **3g** is described and shows properties characteristic of a thiapentalene structure; *i.e.* long N-S-N bonds (1.85 and 1.975 Å) in a nearly linear arrangement (164°) and comprising a heterobicycle which is strictly planar.

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Many X-ray crystallographic studies of 1,6,6aλ⁴-trithiapentalenes **1a** have been reported because of their peculiar S-S-S bonding properties [1]. The aza analogues **1b** are also known, but have been much less studied. Crystal structures are available for 6aλ⁴-thia-1,6-diazapentalenes [2], 6aλ⁴-thia-1,2,5,6-tetraazapentalenes [3] and 6aλ⁴-thia-1,3,4,6-tetraazapentalenes [4], and they all indicate long S-N bond lengths varying between 1.78 and 1.97 Å. Benzo bridging was shown to destroy the thiapentalenic properties [5].

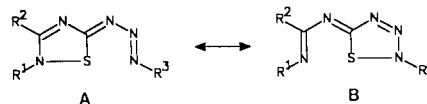


Some time ago we reported briefly on the synthesis of three 6aλ⁴-thia-1,2,3,4,6-pentaazapentalenes **3a-c** by reacting 5-imino-Δ³-1,2,4-thiadiazolines **2** with *p*-nitrobenzenediazonium tetrafluoroborate in the presence of pyridine [6]. These products, however, were not suitable for X-ray crystallographic analysis. In order to gain insight into the structural properties of such molecules, we have continued our research in this field and prepared the derivatives **3d-g** by the same method.



	R ¹	R ²	R ³
a	Ph	Ph	<i>p</i> -NO ₂ C ₆ H ₄
b	<i>p</i> -MeC ₆ H ₄	<i>i</i> -Pr	<i>p</i> -NO ₂ C ₆ H ₄
c	Me	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -NO ₂ C ₆ H ₄
d	Me	Ph	<i>p</i> -NO ₂ C ₆ H ₄
e	PhCH ₂	Ph	<i>p</i> -NO ₂ C ₆ H ₄
f	Me	Ph	<i>p</i> -BrC ₆ H ₄
g	PhCH ₂	Ph	<i>p</i> -BrC ₆ H ₄

These thiaazapentalenes can be described by the dual canonical forms **A** and **B** and the question which needs to be addressed is which of **A** or **B** contributes most to the real structure of the compounds. From a consideration of the basicity of the amidine *versus* the triazene side-chain, resonance form **A** is expected to have the lowest energy content. This was indeed found to be the case.



Compound **3g** was selected for our X-ray crystallographic analysis and the results are shown in Figure 1. The heterobicycle is strictly planar with a maximum deviation from the best plane through the eight atoms 1-8 of only 0.009 Å. The bromophenyl ring is twisted 0.12°, and the phenyl ring 15.6° out of this plane. The N2-S1-N8 atoms approach the colinear arrangement, 164°, which is favorable for an electron-rich three-center bonding [7].

The S1-N2 bond is shorter than S1-N8 and both are significantly longer than the normal covalent S-N bond length of 1.74 Å, yet much shorter than the corresponding van der Waals distance of 3.35 Å. The covalent bond strength can be estimated from Huggins' equation (1) [8]:

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

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. Compound **3g** has S-N distances much shorter than the Huggins constant energy distance of 2.58 Å, indicating strong covalent bonding. The calculated dissociation energies are 29 kcal/mole for S1-N2 and 16 kcal/mole for S1-N8. These values are comparable with those of other thiaazapentalenes [9].

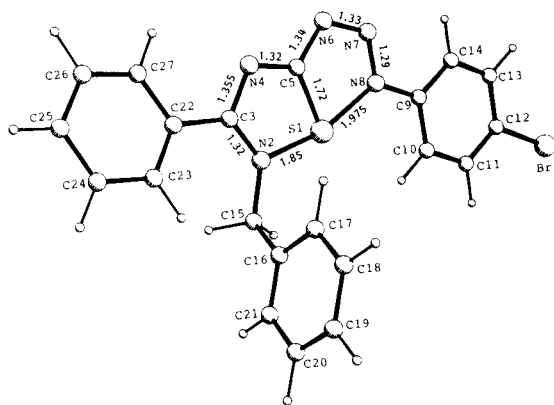


Figure 1. Molecular structure of **3g** with arbitrary numbering scheme and selected bond lengths.

Table 1

Atomic Coordinates ($\times 10^4$) and Equivalent Temperature Factors (\AA^2) ($\times 10^3$) of **3g**

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i^* a_j^*$$

	x	y	z	U_{eq}
S1	629(1)	9473(1)	7070(1)	44(1)
N2	1230(3)	8490(2)	6209(2)	46(1)
C3	-435(4)	8413(2)	5672(2)	43(1)
N4	-2188(4)	9059(2)	5850(2)	49(1)
C5	-1849(4)	9629(2)	6556(3)	49(1)
N6	-3360(4)	10323(3)	6867(3)	64(1)
N7	-2739(4)	10817(3)	7584(2)	62(1)
N8	-790(4)	10549(2)	7832(2)	49(1)
C9	32(4)	11036(2)	8576(2)	48(1)
C10	2135(5)	10750(3)	8839(3)	60(1)
C11	2996(5)	11221(3)	9571(3)	61(1)
C12	1793(5)	11956(3)	10038(3)	56(1)
C13	-303(5)	12269(3)	9777(3)	68(1)
C14	-1160(5)	11807(3)	9047(3)	63(1)
C15	3358(4)	7969(2)	6210(3)	51(1)
C16	3796(4)	6806(2)	7019(2)	45(1)
C17	2377(5)	6381(3)	7774(3)	56(1)
C18	2866(6)	5322(3)	8537(3)	70(1)
C19	4796(7)	4698(3)	8528(3)	79(1)
C20	6194(6)	5124(3)	7773(3)	74(1)
C21	5711(5)	6182(3)	7015(3)	61(1)
C22	-585(5)	7690(2)	4919(2)	48(1)
C23	874(6)	6806(3)	4860(3)	72(1)
C24	631(9)	6185(4)	4139(4)	96(2)
C25	-1167(8)	6396(4)	3495(4)	81(2)
C26	-2625(6)	7285(3)	3559(3)	64(1)
C27	-2345(5)	7938(3)	4245(2)	53(1)
Br	2988(1)	12582(0)	11037(0)	72(0)

EXPERIMENTAL

The synthesis of compounds **3a,b,c** is reported in our preliminary communication [6].

Table 2
Bond Lengths (\AA) of **3g**

N2 -S1	1.847(3)	C5 -S1	1.723(3)
N8 -S1	1.975(2)	C3 -N2	1.323(4)
C15 -N2	1.449(3)	N4 -C3	1.355(3)
C22 -C3	1.491(4)	C5 -N4	1.323(4)
N6 -C5	1.343(4)	N7 -N6	1.326(4)
N8 -N7	1.293(3)	C9 -N8	1.402(4)
C10 -C9	1.394(4)	C14 -C9	1.402(4)
C11 -C10	1.389(5)	C12 -C11	1.370(5)
C13 -C12	1.391(5)	Br -C12	1.888(3)
C14 -C13	1.378(5)	C16 -C15	1.518(4)
C17 -C16	1.374(4)	C21 -C16	1.377(4)
C18 -C17	1.403(5)	C19 -C18	1.386(5)
C20 -C19	1.364(6)	C21 -C20	1.398(5)
C23 -C22	1.366(5)	C27 -C22	1.396(4)
C24 -C23	1.371(6)	C25 -C24	1.398(7)
C26 -C25	1.371(6)	C27 -C26	1.370(5)

Table 3

Bond Angles ($^\circ$) of **3g**

C5 -S1 -N2	84.3(1)	N8 -S1 -N2	164.2(1)
N8 -S1 -C5	79.9(1)	C3 -N2 -S1	111.3(2)
C15 -N2 -S1	117.2(2)	C15 -N2 -C3	131.5(3)
N4 -C3 -N2	115.2(2)	C22 -C3 -N2	127.3(2)
C22 -C3 -N4	117.5(2)	C5 -N4 -C3	111.2(2)
N4 -C5 -S1	118.0(2)	N6 -C5 -S1	119.9(2)
N6 -C5 -N4	122.1(3)	N7 -N6 -C5	113.7(2)
N8 -N7 -N6	113.5(2)	N7 -N8 -S1	113.0(2)
C9 -N8 -S1	128.9(2)	C9 -N8 -N7	118.1(2)
C10 -C9 -N8	118.1(3)	C14 -C9 -N8	122.9(3)
C14 -C9 -C10	119.0(3)	C11 -C10 -C9	119.5(3)
C12 -C11 -C10	120.5(3)	C13 -C12 -C11	121.2(3)
Br -C12 -C11	119.9(2)	Br -C12 -C13	118.9(3)
C14 -C13 -C12	118.4(3)	C13 -C14 -C9	121.4(3)
C16 -C15 -N2	113.3(2)	C17 -C16 -C15	122.2(2)
C21 -C16 -C15	118.4(3)	C21 -C16 -C17	119.4(3)
C18 -C17 -C16	120.6(3)	C19 -C18 -C17	119.7(3)
C20 -C19 -C18	119.3(3)	C21 -C20 -C19	121.0(3)
C20 -C21 -C16	120.0(3)	C23 -C22 -C3	124.1(3)
C27 -C22 -C3	117.2(3)	C27 -C22 -C23	118.8(3)
C24 -C23 -C22	120.6(3)	C25 -C24 -C23	120.9(4)
C26 -C25 -C24	118.0(3)	C27 -C26 -C25	121.1(3)
C26 -C27 -C22	120.5(3)		

6-Methyl-1-(*p*-nitrophenyl)-5-phenyl-6a λ^4 -thia-1,2,3,4,6-pentaazapentalene (**3d**).

To an ice-cooled solution of 2-methyl-3-phenyl- Δ^3 -1,2,4-thiadiazolin-5-imine (**2**, $R^1 = \text{Me}$, $R^2 = \text{Ph}$) (500 mg, 2.6 mmol) [10] and one equivalent of *p*-nitrobenzenediazonium tetrafluoroborate (620 mg) in tetrahydrofuran (20 ml) was added dropwise pyridine (5 ml). The reaction mixture was stirred overnight at room temperature. The precipitate was collected and washed with chloroform to give **3d** in 88% yield (780 mg), mp 265 $^\circ$ (acetonitrile); this compound was too poorly soluble for nmr analysis; ms: (%) m/z 340 (6, M^+), 312 (6.5, $M^+ - N_2$), 190 (7, $M^+ - NO_2C_6H_4N_2$), 150 (100, $NO_2C_6H_4N_2$), 129 (26, $PhCNCN^+$), 122 (83, $NO_2C_6H_4^+$), 118 (61), 104 (16), 92 (13).

Anal. Calcd. for $C_{15}H_{12}N_6O_2S$ (mol wt 340): C, 52.94; H, 3.53. Found: C, 52.69; H, 3.59.

6-Benzyl-1-(*p*-nitrophenyl)-5-phenyl- $6a\lambda^4$ -thia-1,2,3,4,6-pentaazapentalene (**3e**).

To an ice-cooled solution of 2-benzyl-3-phenyl- Δ^3 -1,2,4-thiadiazolin-5-imine (**2**, $R^1 = \text{PhCH}_2$, $R^2 = \text{Ph}$) (500 mg, 2 mmoles) [10] and one equivalent of *p*-nitrobenzenediazonium tetrafluoroborate (444 mg) in tetrahydrofuran (20 ml) was added dropwise pyridine (5 ml). The reaction mixture was stirred overnight at room temperature and then poured into water. The precipitate was filtered off, washed with water and chromatographed on silica gel with carbon tetrachloride/ethyl acetate (3:1) as the eluent to give **3e** in 65% yield (510 mg), mp 197° (acetonitrile); ^1H nmr (250 MHz, deuteriochloroform): δ 5.3 (s, 2H, CH_2), 7.2-7.75 (4 m, 10H, 2 Ph), 7.85 and 8.3 (two d, 4H, $p\text{-NO}_2\text{C}_6\text{H}_4$); ^{13}C nmr (deuteriochloroform): δ 49.4 (CH_2), 120.4, 125.3, 127.2-131.5, 136.5, 146.4 and 147.1 (aromatic C-atoms), 163.4 ($\text{PhC}=\text{N}$), 166.9 (SCN); ms: (%) m/z 416 (4, M^+), 388 (5, M^+-N_2), 150 (50, $\text{NO}_2\text{C}_6\text{H}_4\text{N}_2^+$), 122 (34, $\text{NO}_2\text{C}_6\text{H}_4^+$), 91 (100, C_7H_7^+).

Anal. Calcd. for $\text{C}_{21}\text{H}_{16}\text{N}_6\text{O}_2\text{S}$ (mol wt 416): C, 60.58; H, 3.85. Found: C, 60.44; H, 3.76.

1-(*p*-Bromophenyl)-6-methyl-5-phenyl- $6a\lambda^4$ -thia-1,2,3,4,6-pentaazapentalene (**3f**).

To a solution of **2** ($R^1 = \text{Me}$, $R^2 = \text{Ph}$) (500 mg, 2.6 mmoles) in tetrahydrofuran (20 ml) was added at -20° one equivalent of *p*-bromobenzenediazonium tetrafluoroborate (710 mg) and pyridine (3 ml). After stirring for 3 days at 5° , the precipitate was filtered off and washed with ether to give **3f** in 27% yield (265 mg), mp 226-228° (chloroform/methanol, 1:2); ^1H nmr (250 MHz, deuteriochloroform): δ 3.67 (s, 3H, Me), 7.55 and 7.7 (two d, 4H, $p\text{-BrC}_6\text{H}_4$), 7.5-7.85 (two m, 5H, Ph); ^{13}C nmr (deuteriochloroform): δ 31.5 (Me), 121.5-132.7 and 141.2 (aromatic C-atoms), 162.1 ($\text{PhC}=\text{N}$), 166.5 (SCN); ms: (%) m/z 373/375 (5, M^+), 345/347 (4, M^+-N_2), 190 (4, $\text{M}^+-\text{BrC}_6\text{H}_4\text{N}_2^+$), 183/185 (71, $\text{BrC}_6\text{H}_4\text{N}_2^+$), 155/157 (60, BrC_6H_4^+), 129 (21, PhCNCN^+), 118 (100), 103 (10, PhCN^+).

Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{BrN}_5\text{S}$ (mol wt 374): C, 48.13; H, 3.21. Found: C, 48.03; H, 3.17.

6-Benzyl-1-(*p*-bromophenyl)-5-phenyl- $6a\lambda^4$ -thia-1,2,3,4,6-pentaazapentalene (**3g**).

To an ice-cooled solution of **2** ($R^1 = \text{PhCH}_2$, $R^2 = \text{Ph}$) (500 mg, 2 mmoles) and one equivalent of *p*-bromobenzenediazonium tetrafluoroborate (507 mg) in tetrahydrofuran (20 ml) was added dropwise pyridine (3 ml). After stirring the reaction mixture overnight at room temperature, tetrahydrofuran was replaced by chloroform (20 ml) and the solution was washed with diluted hydrochloric acid (3 x 10 ml). The organic layer was dried over magnesium sulfate and chromatographed on silica gel with carbon tetrachloride/ethyl acetate (3:1) as the eluent to give **3g** in 33% yield (280 mg), mp 175° (dichloromethane/hexane, 3:1); ^1H nmr (250 MHz, deuteriochloroform): δ 5.2 (s, 2H, CH_2), 7.15-7.7 (m, 14 aromatic H); ^{13}C nmr (deuteriochloroform): δ 49.0 (CH_2), 121.8-132.8, 137.2 and 141.0 (aromatic C-atoms), 163.2 ($\text{PhC}=\text{N}$), 167.1 (SCN); ms: (%) m/z 449/451 (1, M^+), 421/423 (1, M^+-N_2), 183/185 (22, $\text{BrC}_6\text{H}_4\text{N}_2^+$), 155/157 (17, BrC_6H_4^+), 91 (100, C_7H_7^+).

Anal. Calcd. for $\text{C}_{21}\text{H}_{16}\text{BrN}_5\text{S}$ (mol wt 450): C, 56.00; H, 3.56. Found: C, 55.86; H, 3.53.

Crystal Structure Analysis of **3g**.

Compound **3g** crystallizes in the triclinic space group P-1 with $a = 6.531(1)$, $b = 12.368(1)$, $c = 12.737(1)$ Å, $\alpha = 74.25(1)$, $\beta = 88.95(1)$, $\gamma = 82.09(1)^\circ$, $V = 980.6(2)$ Å³, $Z = 2$, $D_x = 1.53$ gcm⁻³. Intensities from a parallelepiped crystal 0.5 x 0.3 x 0.15 mm were measured using a Huber 4-circle diffractometer with graphite-monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.54178$ Å). Of the 3523 independent reflections with $\sin\theta/\lambda \leq 0.60$ Å⁻¹, 3170 had $I \geq 2.5 \sigma(I)$ and were considered as observed. The structure was solved by direct methods (SHELXS-86) [11] and refined by least squares methods [12] to an R-value of 0.057 for the observed reflections. Atomic coordinates, bond lengths and angles are given in Tables 1, 2 and 3. Figure 1 shows a view of the molecule with an arbitrary non systematic numbering scheme and selected bond lengths.

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